

Effect of Water-Solids Ratio on the Compressive Strength, Degree of Reaction and
Microstructural Characterization of Fly Ash-Waste Glass-Based Geopolymers

A Thesis
SUBMITTED TO THE FACULTY OF
UNIVERSITY OF MINNESOTA
BY

Matthew S. Jansen

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Dr. Mary Christiansen

April 2017

Acknowledgements

I would like to thank Dr. Mary Christiansen, Kyrstyn Haapala, and other graduate and undergraduate students at the University of Minnesota Duluth. Their support and guidance throughout my research kept me focused and motivated. It seemed like Dr. Christiansen was always available when a question would come up or an unexpected result came forth, and if she wasn't, I could always ask Kyrstyn what she would think. It was also very helpful when fellow students would assist in mixing and casting samples. Without the help I received, this thesis process would not have gone as smoothly, nor would it have been as fun, and for this I am grateful. Thank you!

Dedication

I'd like to dedicate this thesis to my friends and family.

Abstract

On a global scale, the production of portland cement is responsible for approximately 5% of carbon emissions. In an effort to reduce carbon emissions, alternative binders are being implemented into the cement industry. Geopolymer technology combines aluminosilicate sources with an alkali solution to create a binder that has the potential to completely eliminate the need for portland cement in concrete. There has been limited research regarding the effect that the water-solids ratio (similar to water-cement ratio) has on geopolymer performance. For that reason, this research focused on the effect of the water-solids ratio on compressive strength, degree of reaction, and microstructure of fly ash – waste glass-based geopolymer mortars. Geopolymer mortars made of varying levels of fly ash and waste glass were produced. Three water-solids ratios were examined for each mixture, and compressive strength, degree of reaction, and microstructure characteristics were investigated in an effort to discover trends. Results showed that the water-solids ratio had an effect on compressive strength, but not a significant effect on degree of reaction. When comparing mixture compositions, mixtures containing fly ash seemed to be more sensitive to the water-solids ratio. Unreacted particles and different types of zeolites, depending on the mixture composition, were observed during microstructural analysis. Locations where particles seemed to have been “pulled-out” of the geopolymer paste were also observed in mixtures with higher water-solids ratios. However, more research is required to confirm these conclusions.

Table of Contents

List of Tables	vii
List of Figures	viii
1 Introduction	1
1.1 Motivation	1
1.2 Project Goals	1
2 Literature Review	4
2.1 Portland Cement Concrete	5
2.1.1 United States Infrastructure	5
2.1.2 Portland Cement Concrete	6
2.1.3 Environmental Concerns	7
2.1.4 Concrete Mixture Design	7
2.1.5 Portland Cement Production	8
2.1.6 Portland Cement Chemistry	10
2.2 The Role of Water in Portland Cement Concrete	14
2.2.1 Water-Cement Ratio	16
2.2.2 Curing Requirements	18
2.3 Geopolymer Concrete	19
2.3.1 Introduction	19
2.3.2 Environmental Benefits	20
2.3.3 Chemical and Mechanical Properties	20
2.3.4 Obstacles	22
2.4 Geopolymer Production	24
2.4.1 Materials	24
2.4.2 Reaction Mechanisms	25
2.4.3 Effect of Activator Composition on Geopolymerization	28
2.4.4 Effect of Elemental Oxide Stoichiometry on Reaction Mechanisms	29
2.4.5 Comparison of Geopolymer and Portland Cement	31
2.5 The Role of Water in Geopolymers	32
2.5.1 Water-Solids Ratio	33
2.5.2 Zeolites	34
2.5.3 Curing Requirements	35
2.6 Literature Review Summary	35
3 Materials and Experimental Methods	39
3.1 Experimental Plan	39
3.1.1 Phase I – Compressive Strength	39
3.1.2 Phase II – Degree of Reaction	40
3.1.3 Phase III – Microstructural Analysis	40
3.2 Materials	41
3.2.1 Waste Glass	41
3.2.2 Fly Ash	43
3.2.3 Sodium Hydroxide	47
3.2.4 Sodium Silicate	48

3.2.5	Aggregate	49
3.3	Proportioning and Mixing	49
3.3.1	Mixture Stoichiometry	51
3.3.2	Mortar Mixing	53
3.3.3	Paste Mixing	54
3.4	Experimental Procedures.....	55
3.4.1	Compressive Strength	55
3.4.2	Degree of Reaction	56
3.4.3	Microstructural Characterization	58
4	Results and Discussion	60
4.1	100% Glass (100G)	60
4.1.1	100G: Compressive Strength	60
4.1.2	100G: Degree of Reaction	61
4.1.3	100G: Microstructural Analysis.....	62
4.2	75% Glass, 25% Fly Ash (75G25FA).....	63
4.2.1	75G25FA: Compressive Strength	63
4.2.2	75G25FA: Degree of Reaction	65
4.2.3	75G25FA: Microstructural Analysis.....	66
4.3	50% Glass, 50% Fly Ash (50G50FA).....	67
4.3.1	50G50FA: Compressive Strength	67
4.3.2	50G50FA: Degree of Reaction	69
4.3.3	50G50FA: Microstructural Analysis.....	69
4.4	25% Glass, 75% Fly Ash (25G75FA).....	70
4.4.1	25G75FA: Compressive Strength	70
4.4.2	25G75FA: Degree of Reaction	72
4.4.3	25G75FA: Microstructural Analysis.....	73
4.5	100% Fly Ash (100FA)	74
4.5.1	100FA: Compressive Strength	74
4.5.2	100FA: Degree of Reaction	76
4.5.3	100FA: Microstructural Analysis	76
4.6	Mixture Composition Comparison.....	77
4.6.1	Compressive Strength	77
4.6.2	Degree of Reaction	79
4.6.3	Microstructural Analysis.....	81
4.7	Sodium Silicate Mixtures	84
4.8	Unreacted Particles	88
4.9	Zeolites	90
5	Conclusions and Discussion	92
5.1	Compressive Strength	93
5.2	Degree of Reaction	94
5.3	Microstructural Analysis	94
5.4	Mixture Composition	95
5.5	Summary and Future Research	95
6	References	98

7	Appendix A.....	101
---	-----------------	-----

List of Tables

Table 2.1: 2013 Report card for America's infrastructure (ASCE, American Society of Civil Engineers 2013).	6
Table 2.2: Cement chemist notation definitions.	11
Table 2.3: Typical composition of normal portland cement (Mindess, Young, Darwin 2002).	13
Table 2.4: Typical chemical composition (weight percentage) and fineness of other cement types (Mamlouk and Zaniewski 2011).	14
Table 2.5: Comparison of portland cement concrete and geopolymer concrete.....	32
Table 3.1: Mixture compositions used to evaluate the effect of the water-solids ratio. ...	39
Table 3.2: Chemical composition of the glass used in this research by weight percent oxide (Wyoming Analytical Laboratories 2014). Typical soda-lime glass content is included for comparison.	43
Table 3.3: Chemical composition of Class F fly ash used in this research by weight percent oxide (Wyoming Analytical Laboratories 2014).	46
Table 3.4: Chemical composition of activator solutions by weight percent oxide.....	49
Table 3.5: Mixture compositions used to investigate water-solids ratio.	50
Table 3.6: Example of 50% glass, 50% fly ash mixture design.	51
Table 4.1: Degree of reaction results for the 100G mixtures.....	62
Table 4.2: Degree of reaction results for 75G25FA mixtures.	66
Table 4.3: Degree of reaction results for 50G50FA mixtures.	69
Table 4.4: Degree of reaction results for 25G75FA mixtures.	73
Table 4.5: Degree of reaction results for 100FA mixtures.	76
Table 4.6: Comparison between degree of reaction (DOR) and 7-day compressive strength.....	81
Table 4.7: Comparison between degree of reaction (DOR) and 7-day compressive strength of sodium silicate mixtures.	85

List of Figures

Figure 2.1: Cement production flow diagram (Mamlouk and Zaniewski 2011).	9
Figure 2.2: Conditions and reactions inside rotary cement kiln (Mindess, Young, Darwin 2002).	12
Figure 2.3: Cement hydration rate and stages over time (Thomas and Jennings 2008). ..	15
Figure 2.4: Volume relationships as w/c increases (Mindess, Young, Darwin 2002).	17
Figure 2.5: Effect of moist curing on strength gain in PCC concrete (Kosmatka and Wilson 2011).	19
Figure 2.6: Simplified model for geopolymer reaction mechanism (Duxson et al. May 2007).	26
Figure 2.7: Sodium carbonate forming on outside of preliminary geopolymer mixtures, demonstrating what happens when the Na/Al ratio is too high.	30
Figure 2.8: Zeolites observed during microstructural analysis.	34
Figure 3.1: Ground glass powder used in research.	41
Figure 3.2: Particle size distribution graph of waste glass used.	42
Figure 3.3: Class F fly ash.	44
Figure 3.4: Particle size distribution of fly ash used.	45
Figure 3.5: Silica, alumina, and calcium oxides in the source materials used in this research (Graham and Midgley 2000)	47
Figure 3.6: NaOH flake used to make alkali-activating solution.	48
Figure 3.7: Si/Al and Na/Al molar ratios of mortars.	52
Figure 3.8: Geopolymer mortar mixing.	54
Figure 3.9: Humboldt compressive strength testing machine.	56
Figure 3.10: Degree of reaction test setup.	57
Figure 3.11: JEOL JSM-6490LV scanning electron microscope.	59
Figure 4.1: Compressive strength curve for 100G mixtures.	61
Figure 4.2: Examples of the microstructure of the three 100G mixtures.	63
Figure 4.3: Compressive strength curve for 75G25FA mixtures.	64
Figure 4.4: Examples of the microstructure of the 75G25FA mixtures.	67
Figure 4.5: Compressive strength curve for 50G50FA mixtures.	68
Figure 4.6: Examples of the microstructure of the 50G50FA mixtures.	70
Figure 4.7: Compressive strength curve for 25G75FA mixtures.	71
Figure 4.8: Examples of the microstructure of the 25G75FA mixtures.	74
Figure 4.9: Compressive strength curves for 100FA mixtures.	75
Figure 4.10: Examples of the microstructure of the 100FA mixtures.	77
Figure 4.11: Compressive strength trends as water-solids ratio changes in mixtures at 7 days.	78
Figure 4.12: Degree of reaction vs 7-day compressive strength.	80
Figure 4.13: Microstructural comparisons between mixture compositions.	82
Figure 4.14: Degree of reaction vs. 7-day compressive strength of sodium silicate mixtures.	85
Figure 4.15: Sodium hydroxide DOR results compared to sodium silicate DOR results.	86

Figure 4.16: Phases observed during microstructural analysis of sodium silicate mixtures that were not observed during analysis of NaOH-activated mixtures.	87
Figure 4.17: Unreacted glass (A, B), fly ash (C, D), and metakaolin (E, F) particles observed during microstructural analysis.	89
Figure 4.18: Variety of zeolites observed during microstructural analysis.	91

1 Introduction

1.1 Motivation

The production of portland cement is responsible for around 5% of global carbon emissions annually (Huntzinger and Eatmon 2009; Provis and vanDeventer 2009; Shi, Jimenez, Palomo 2011; Sun and Wu 2013). This and other drivers have researchers searching for more eco-friendly alternative binders. The production of geopolymer cement emits significantly less carbon dioxide and geopolymers can achieve similar mechanical and engineering properties to portland cement concrete. Geopolymers are created when an aluminosilicate powder is activated with an alkaline solution. The potential use of geopolymers in the construction industry has raised many questions including how they work, how they perform, and how changing mixture proportioning affects performance. While there are still many unknowns about geopolymers, initial research has shown that these alternative binders possess great potential.

1.2 Project Goals

Many studies either use one aluminosilicate blend and one water-solids ratio to compare a different activator or mixture design ratio. Other studies use different aluminosilicate blends and different water-solids ratios to compare properties and performance (Jang, Lee, Lee 2014; Sofi et al. 2007; Steveson and Sagoe-Crentsil 2005). However, it is very difficult to directly compare properties between mixture compositions using different water-solids ratios. In other words, the water-solids ratio could be what affects the

properties of interest. Therefore, the goal of this project was to investigate how changing the water-solids ratio affects the compressive strength, degree of reaction, and microstructure of fly ash-waste glass-based geopolymers.

Compressive strength in ordinary portland cement concrete is strongly affected by the water-cement ratio. Within reasonable workability and hydration limits, a lower water-cement ratio results in higher strengths due to fewer capillary pores, and a higher water-cement ratio leads to lower compressive strength as a result of an increase in voids (Mindess, Young, Darwin 2002). The primary question this research aimed to answer was: **Does the water-solids ratio in geopolymers have the same effect on compressive strength as the water-cement ratio in ordinary portland cement concrete?** It was expected that the water-solids ratio in geopolymers would have the same effect on geopolymer compressive strength as the water-cement ratio does in portland cement concrete.

A secondary question was: How does changing the water-solids ratio affect degree of reaction (how well dissolution occurs)? On one hand, increasing the water-solids ratio increases the amount of liquid available for dissolution. On the other hand, too much water can dilute the activating solution. However, it was expected that the degree of reaction would correlate with compressive strength. That is to say, mixtures with higher degrees of reaction were expected to have higher compressive strengths.

Another secondary research question was: How does changing the water-solids ratio affect the microstructure of geopolymers? It was expected that in mixtures with higher water-solids ratios, microstructures would be less homogeneous and more unreacted particles and zeolites would be present.

The final question this research aimed to answer was: Are trends consistent when changing aluminosilicate sources? It was expected that any trends noted in the above phases of this research would be similar across all mixture compositions.

Three water-solids ratios were examined for five mixture compositions of varying amounts of fly ash and waste glass. For each set of samples, the compressive strength and degree of reaction were measured and the samples were examined under a scanning electron microscope (SEM).

2 Literature Review

The literature review is broken up into five sections, beginning with the history and current use of portland cement and ending with the production and future potential of geopolymer technology. Brief summaries of the importance and relevance of each section are as follows:

2.1 Portland Cement Concrete - This section covers the production and use of portland cement and portland cement concrete. It is important to cover because geopolymer production and performance will be compared to portland cement.

2.2 The Role of Water in Portland Cement Concrete - This section discusses the role water plays in portland cement concrete and touches on the water-cement ratio, hydration, and curing. It is important to discuss these topics because the water-solids ratio in geopolymers is very similar to the water-cement ratio in portland cement concrete. In order to compare how water affects geopolymers, the effects that water has on portland cement must be understood.

2.3 Geopolymer Concrete - This section introduces geopolymer technology and discusses performance results from other studies.

2.4 Geopolymer Production - This section walks through the production of geopolymers. It is a very different production process from portland cement and is important to understand the difference.

2.5 The Role of Water in Geopolymers - This section discusses the role water plays in geopolymer concrete. It discusses the water-solids ratio and the role of water in the

production process and phase formation during geopolymerization. This section is the basis of the research discussed in this paper.

2.1 Portland Cement Concrete

2.1.1 United States Infrastructure

Every four years, the American Society of Civil Engineers (ASCE) evaluates America's infrastructure and releases *ASCE's Report Card for America's Infrastructure* (ASCE, American Society of Civil Engineers 2013). Infrastructure grades in 2013, shown in Table 2.1, were assigned based on the "capacity and condition of current infrastructure, current and estimated funding necessary for improvement, future need, operation and maintenance, public safety, resilience to failure, and innovation" (ASCE, American Society of Civil Engineers 2013).

As Table 2.1 indicates, America's infrastructure is not in good shape. Since 1998, grades have been near failing due to delayed maintenance and a lack of investment. Material selection and material production are two processes worth investing in to fix this issue. Portland cement concrete is the primary construction material used in many of the categories listed in Table 2.1. The following sections provide a brief overview of current portland cement concrete use today.

Table 2.1: 2013 Report card for America's infrastructure (ASCE, American Society of Civil Engineers 2013).

CATEGORY	GRADE
Aviation	D
Bridges	C +
Dams	D
Drinking Water	D
Energy	D +
Hazardous Waste	D
Inland Waterways	D –
Levees	D –
Ports	C
Public Parks and Recreation	C –
Rail	C +
Roads	D
Schools	D
Solid Waste	B –
Transit	D
Wastewater	D
America's Cumulative G.P.A.	D +

2.1.2 Portland Cement Concrete

Every year nearly one ton of portland cement concrete is produced for every person in the world (Huntzinger and Eatmon 2009), making concrete the most widely used infrastructure material on the planet. Many projects, from pavements and parking lots to dams, bridges, and buildings use concrete as a primary building material. The main properties that make concrete such a desirable material include its availability and cost, and the ability to produce components in a variety of shapes and sizes (Kumar Mehta and

Monteiro 2006). It is a unique material in the sense that an engineer can directly influence the quality of the concrete and how well it performs by changing specific parameters of the mixture. Concrete performance also depends heavily on how it is mixed, transported, placed, and cured (Mamlouk and Zaniewski 2011).

2.1.3 Environmental Concerns

One of the primary concerns associated with cement production is CO₂ emissions. According to the International Energy Agency's (IEA) Greenhouse Gas R & D, for every kilogram of cement produced, 0.81 kilograms of carbon dioxide (CO₂) is emitted into the atmosphere (Huntzinger and Eatmon 2009). The production of cement is responsible for roughly 5% of global anthropogenic CO₂ emissions (Huntzinger and Eatmon 2009; Shi, Jiménez, Palomo 2011), making it the third largest source of carbon emissions in the United States (Huntzinger and Eatmon 2009). Due to this pressing environmental issue, alternative technologies are being researched that can replace or supplement the use of portland cement. Geopolymer concrete is one alternative that has potential as a new, strong, and durable binder technology.

2.1.4 Concrete Mixture Design

There are three qualities that the Portland Cement Association (PCA) identifies as important in properly proportioned concrete mixtures: workability, durability and strength, and economy (Mamlouk and Zaniewski 2011). In most cases, strength is the primary tested property. To achieve strength and workability, the proper amount of cement, water, and aggregate must be determined. Mixture designs have been developed

throughout the history of concrete to determine appropriate ratios of concrete ingredients. The absolute volume method is the most accurate method (Kumar Mehta and Monteiro 2006) and is essentially a “cookbook” process due to the large amount of historical data available. Parameters such as air content, workability, and required strength are determined based on service environment, construction type, and structural constraints (Kosmatka and Wilson 2011).

2.1.5 Portland Cement Production

While the materials that make up concrete consist mainly of aggregate (coarse and fine) and mixing water, approximately 10-15% of concrete consists of portland cement. Portland cement is the “glue” that bonds the aggregates together. Some projects may require cement with specific properties, and many of these properties can be achieved by altering the type of cement used in a mixture. For example, a structure that needs to be completed quickly and requires high early strength can be achieved using Type III high early strength cement. There are five different types of portland cement and each varies in chemical composition and fineness (shown in Table 2.3 and Table 2.4 in Section 2.1.6).

Understanding the cement production process can help explain the environmental and economic consequences of manufacturing portland cement. The production process, shown in Figure 2.1, is quite complex and involves various materials, heating techniques, and fuel sources (Huntzinger and Eatmon 2009).

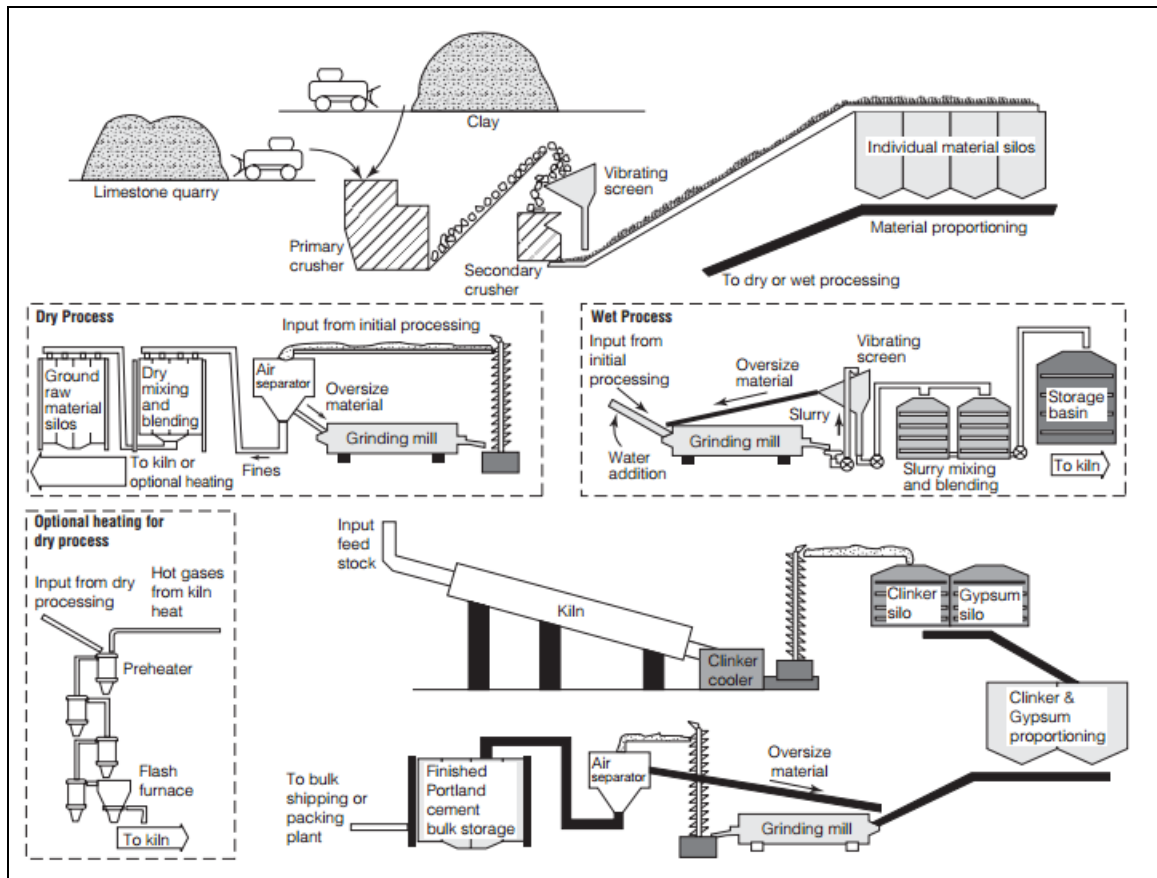


Figure 2.1: Cement production flow diagram (Mamlouk and Zaniewski 2011).

The portland cement production process begins with the mining and transportation of materials rich in calcia and silica, such as limestone and clay, to a crusher where the minerals are ground into a powder and transported to the cement plant. At the cement plant, the powders are blended together based on chemical composition and sent to a preheating tower. The preheating tower helps begin the calcination process, where carbon dioxide (CO_2) is removed from calcium carbonate (CaCO_3) to create calcium oxide, or lime (CaO). When the raw materials reach the bottom of the preheating tower they are about 40% calcined. The materials then enter the precalciner (also referred to as a flash

furnace) where the calcination process nears completion (85-95% calcined). The precalciner accounts for over half of the fuel burned during cement production. After the preheater and precalciner, the materials enter a rotary kiln, where material temperatures can reach up to 1500°C. The calcination process is responsible for about half of the carbon emitted during cement production (Huntzinger and Eatmon 2009), but it is also a crucial step in the process, and necessary for the formation of the main phases of portland cement. The material that comes out of the kiln is cooled rapidly and known as clinker. Once the clinker leaves the kiln, it is interground with gypsum, which is added to help regulate the setting time of concrete.

Around the world, cement is being produced at a rate of approximately four billion tons per year (van Oss 2014). In 2013, the United States alone produced 75.1 million tons of portland cement, where sales totaled \$7.6 billion. Most of the sales went toward the production of concrete products (ready-mix, paving, building materials, etc.), which is a \$45 billion industry (van Oss 2014).

2.1.6 Portland Cement Chemistry

Throughout the cement industry, cement chemist notation is used to represent elemental oxides. Table 2.2 shows the difference compared to using conventional chemical symbols.

Table 2.2: Cement chemist notation definitions.

Element/Oxide	Chemical Symbol	Cement Chemist Notation
Lime	CaO	C
Silica	SiO ₂	S
Alumina	Al ₂ O ₃	A
Ferric Oxide	Fe ₂ O ₃	F
Sulfur Trioxide	SO ₃	S
Water	H ₂ O	H

Portland cement consists of calcia, alumina, silica, iron oxide, and calcium sulfate. There are five major phases in portland cement, with four being created during the calcination and clinkering stages of the production process, shown in Figure 2.2. Each phase plays a significant role in the performance of portland cement concrete.

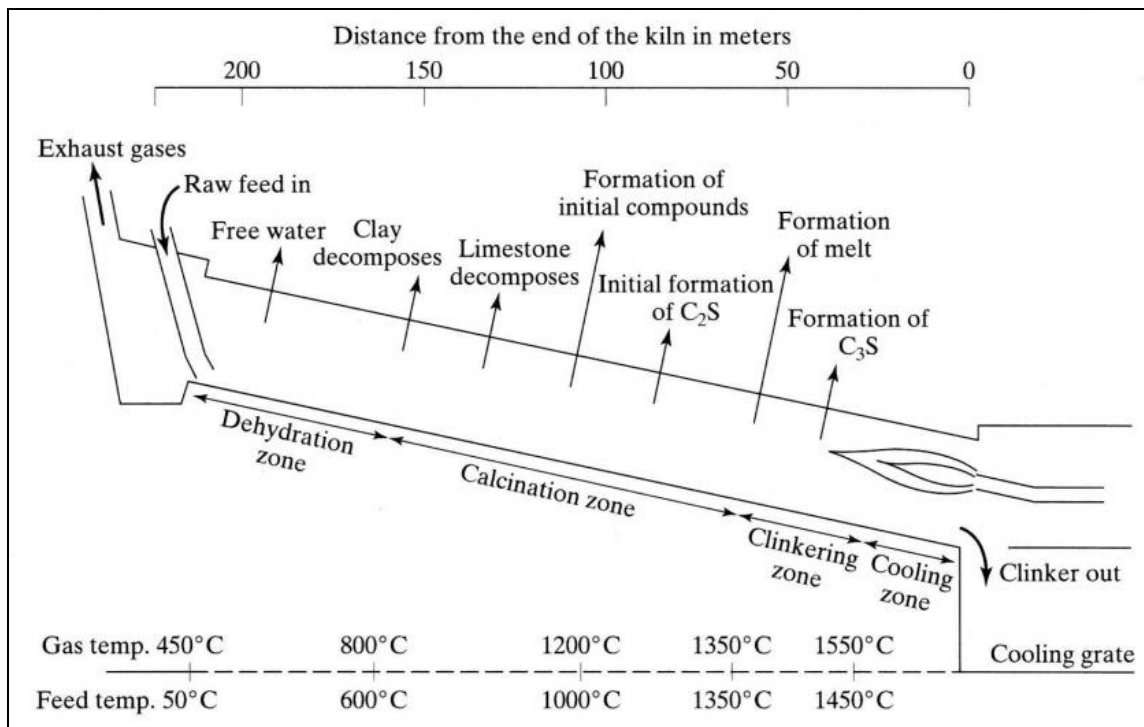


Figure 2.2: Conditions and reactions inside rotary cement kiln (Mindess, Young, Darwin 2002).

Impure tricalcium silicate (C_3S in cement chemist notation), also known as alite, accounts for about 55% by mass in normal (Type I) portland cement, shown in Table 2.3. Alite is responsible for the early strength of the concrete and reacts quickly with water. Impure dicalcium silicate (C_2S), also known as belite, accounts for roughly 18% of normal portland cement and is responsible for the ultimate strength of the concrete. Older cements used to have more belite than alite because early strength was not a primary concern like it is today. The melt in Figure 2.2 refers to tricalcium aluminate (C_3A or aluminate) and tetracalcium aluminoferrite (C_4AF or ferrite), which melts to form a liquid, allowing for the creation of alite at a reduced temperature in the kiln. Ferrite controls the color of the cement. Aluminate has a very high heat of hydration and reacts

extremely fast with water. To account for the reaction rate of the C_3A and to prevent a flash set, gypsum is blended into the mixture.

Table 2.3: Typical composition of normal portland cement (Mindess, Young, Darwin 2002).

Phase	Cement Chemist Notation	Weight Percentage
Tricalcium Silicate	C_3S	55
Dicalcium Silicate	C_2S	18
Tricalcium Aluminate	C_3A	10
Tetracalcium Aluminoferrite	C_4AF	8
Gypsum	$C\bar{S}H_2$	6

As stated in the previous section, there are five types of cements that can be used for specific applications. Type I (normal) cement is used for general concrete work and its composition is shown in Table 2.3. Type II cement (moderate sulfate resistance) is used in applications where moderate sulfate content is present (usually in soil or in water). The lower C_3A content (shown in Table 2.4) improves sulfate resistance. Type III cement is used when high early strength is needed. While the composition of Type III cement is similar to Type I, the average size of the cement particles is much smaller, allowing them to react faster and gain strength much quicker. Type IV cement is used when the volume of concrete used is large and the heat of hydration must be controlled. As shown in Table 2.4, the C_3S and C_3A contents in Type IV cement are much lower than the other types of cement, which causes the cement to react slower and give off less heat. Type V cement is used where high sulfate content is present and has a slightly lower C_3A content compared to Type II cement.

Table 2.4: Typical chemical composition (weight percentage) and fineness of other cement types
(Mamlouk and Zaniewski 2011).

Cement Type	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Blaine Fineness (m ² /kg)
Type II	51	24	6	11	370
Type III	56	19	10	7	540
Type IV	28	49	4	12	380
Type V	38	43	4	9	380

2.2 The Role of Water in Portland Cement Concrete

Portland cement is hydraulic, meaning it will react and harden when it comes into contact with water; these reactions are called hydration reactions. The hydration process begins as soon as portland cement comes into contact with water. The hydration product of interest is calcium-silicate-hydrate (C-S-H) gel, which accounts for concrete's strength and other engineering properties. C-S-H grows out from the cement particles until other cement particles link together (similar to how Velcro works). Calcium hydroxide (CH) is the other primary reaction product from the hydration of calcium silicates, but is not desired because of durability issues.

Water plays two key roles in cement hydration. First, it provides a medium for the cement phases (listed in Table 2.3) to dissolve in during hydration. Second, some of the water is used in the hydration reactions and becomes chemically bound within the hydration products. Hydration reactions occur in two stages: through-solution and solid state, as depicted in Figure 2.3.

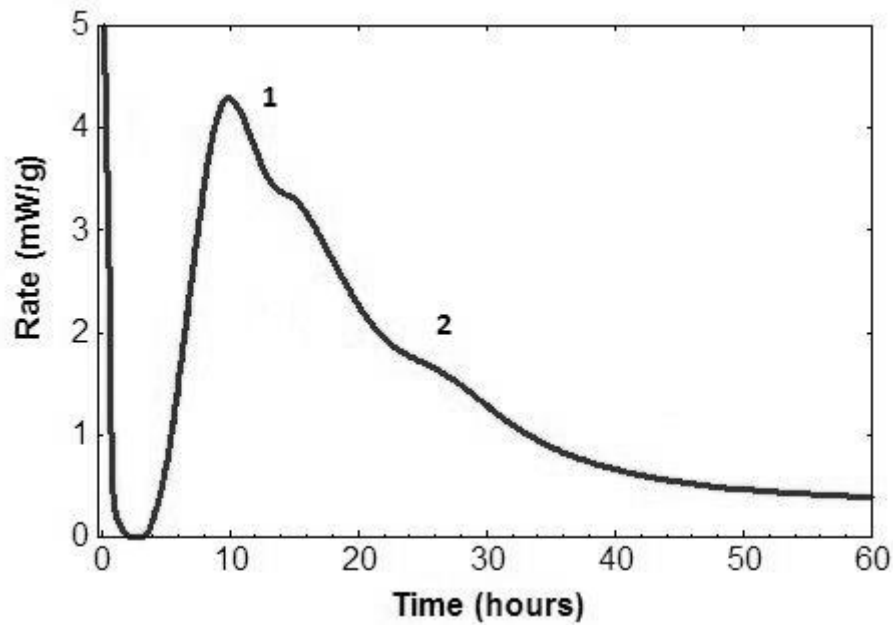


Figure 2.3: Cement hydration rate and stages over time (Thomas and Jennings 2008).

The first stage of hydration is “through-solution” (labeled as “1” in Figure 2.3), which is where reactions occur at the surface of the cement particles (dissolution is a through-solution reaction) and is the dominant mechanism during the early stages of hydration. The second mechanism is solid-state hydration (labeled as “2”), where the reactions occur as water diffuses through the surface of the cement particles to get to the unreacted cement core. The solid-state hydration mechanism occurs in later stages of hydration and can continue for years. Curing concrete requires moisture to continue the solid-state reactions which is very important in the development of desired concrete properties.

2.2.1 Water-Cement Ratio

In the early 1900s, it was determined that the ratio of the weight of water to the weight of cementitious materials (known as the water-cement ratio) directly affects the desirable properties and performance of concrete. In order for hydration to occur, the mixture requires a minimum of 0.22-0.25 kg of water per 1 kg of portland cement (Mamlouk and Zaniewski 2011). However, in order to achieve 100% hydration of the cement paste, the pores within the system must also be filled with water. Therefore, 0.42 is generally accepted as the water-cement ratio where 100% of the portland cement is theoretically hydrated without the addition of admixtures (Mindess, Young, Darwin 2002; Neuwald 2010). However, a water-cement ratio higher than 0.42 will increase permeability in portland cement concrete and decrease compressive strength. Workability requirements generally increase the water-cement ratio as well.

In most cases, as the water-cement ratio of the mixture increases past 0.42, the workability of the mixture improves, but the compressive strength decreases. This happens because excess water increases the porosity in the concrete due to voids left behind by water molecules that have evaporated. This increased porosity or permeability can negatively affect the mixture's durability (Kosmatka and Wilson 2011). Additionally, when too much water is added to a concrete mixture, aggregate particles are likely to segregate and settle out. Drying shrinkage will also occur more in mixtures with higher water-cement ratios, causing cracking (discussed further in Section 2.2.2).

Water-cement ratios below 0.42 generally result in an increase in compressive strength and a decrease in workability, unless water-reducing admixtures are used. This increase in strength is due in large part to the fact that all of the available water is completely used by the cement particles (some particles do not hydrate completely). This decreases the number of capillary pores (see Figure 2.4). However, if the water-cement ratio is too low, there will not be enough water available for the cement to hydrate. The compressive strength will start to decrease due to an abundance of unhydrated cement particles. A lower water-cement ratio is preferred as long as the mixture can still be placed and consolidated properly (Kosmatka and Wilson 2011).

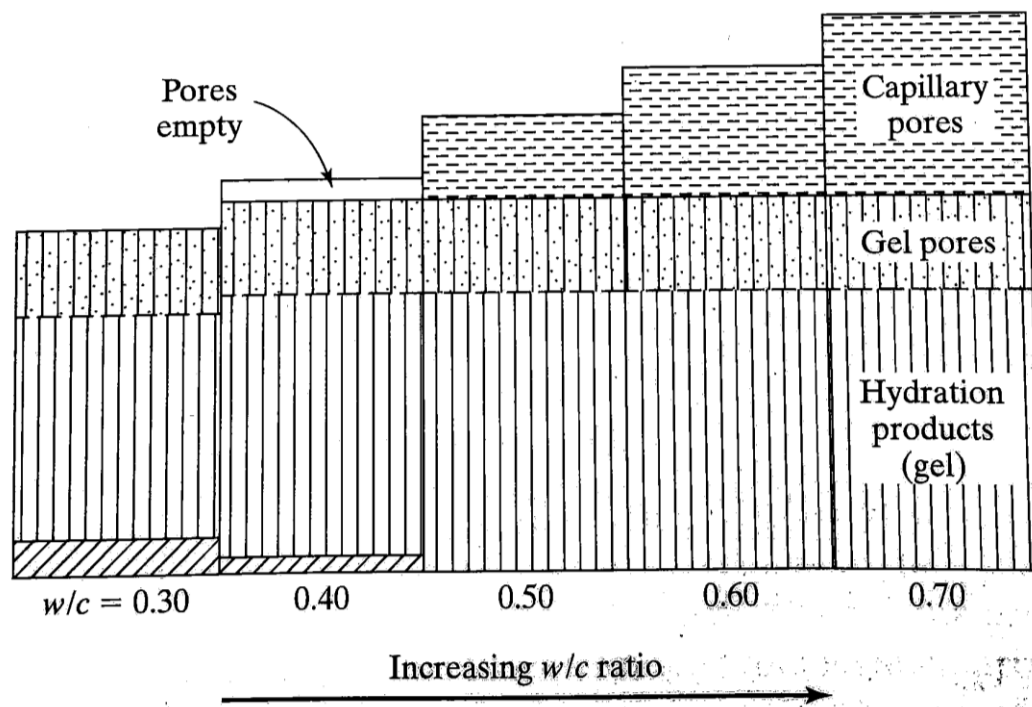


Figure 2.4: Volume relationships as w/c increases (Mindess, Young, Darwin 2002).

2.2.2 Curing Requirements

Adequate moisture and temperature conditions are necessary for concrete to hydrate properly. In order for the cement particles to continue to hydrate, the relative humidity within the concrete must be above 80%. If the relative humidity drops below 80%, hydration will stop, and consequently strength gain will stop (Kosmatka and Wilson 2011; Mamlouk and Zaniewski 2011). Due to this, continuous curing from the time the concrete is placed to the time when the desired properties (strength, durability, shrinkage, etc.) are attained is recommended if practical (Mindess, Young, Darwin 2002). Spraying, ponding, and covering the concrete are some common curing methods, along with curing compounds that can be applied to fresh concrete. The length of time that the concrete mixture is moist cured also affects strength gain, as shown in Figure 2.5. Furthermore, inadequate curing can lead to drying shrinkage, which can lead to a variety of other problems such as cracking, warping, and deflections. The rate at which drying shrinkage occurs is fastest in the early life of the concrete structure. The amount of shrinkage depends on a variety of factors such as size and shape of the structure, the water-cement ratio, steel reinforcement, and more (Mamlouk and Zaniewski 2011).

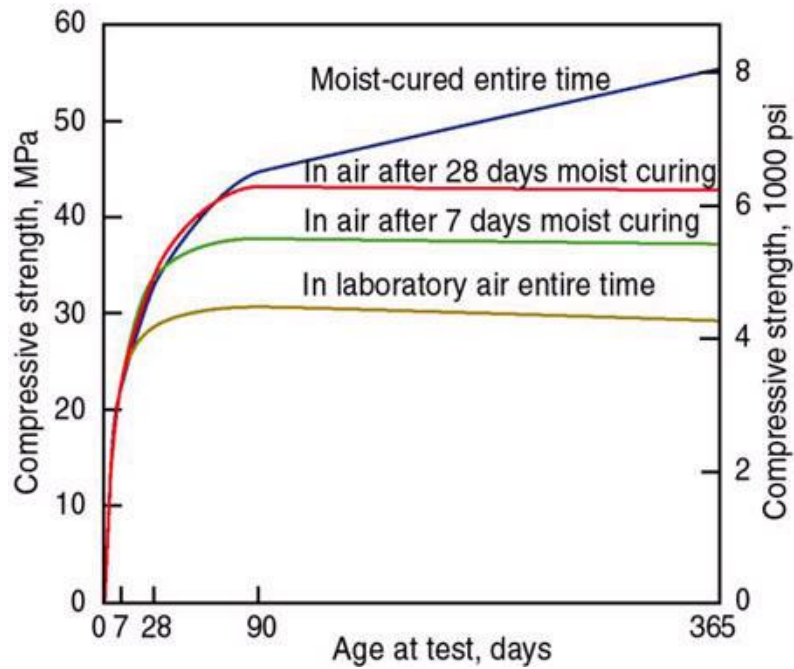


Figure 2.5: Effect of moist curing on strength gain in PCC concrete (Kosmatka and Wilson 2011).

2.3 Geopolymer Concrete

2.3.1 Introduction

Very basically, a geopolymer is a binder formed by the reaction of an aluminosilicate source and an alkaline solution (Provis and vanDeventer 2009). Also known as alkali-activated cements or inorganic polymers (Duxson et al. May 2007), geopolymers can be made from a variety of industrial waste byproducts including fly ash and granulated blast furnace slag, as well as metakaolin (Duxson et al. 2007; Sofi et al. 2007) and waste glass (Christiansen 2013; Cyr, Idir, Poinot 2012; Redden and Neithalath 2014). The ideal precursor materials are amorphous aluminosilicates, meaning materials rich in reactive alumina and silica. When these aluminosilicate sources react with a highly concentrated alkali solution, often in the presence of heat and limited moisture, geopolymers are

created (Duxson et al. May 2007; Duxson et al. 2007). The geopolymerization process is discussed further in 2.4.2.

2.3.2 Environmental Benefits

There are many environmental benefits to using geopolymer concrete. One major advantage that geopolymers have over portland cement is a lower carbon footprint (Duxson et al. 2007). As discussed in Section 2.1.3, carbon emissions are a major concern in regard to portland cement production. In the production of geopolymers, the chemical reaction of calcining calcium carbonate is completely eliminated and the need for kiln heating is significantly reduced or eliminated, thereby significantly reducing CO₂ emissions (Duxson et al. 2007). Another significant advantage geopolymers provide is a market for the use for high volumes of industrial coproducts and byproducts (i.e. fly ash, slag) that would otherwise be disposed of in a landfill. Fly ash, slag, and other byproducts are currently being used in portland cement concrete as supplementary cementitious materials, but not as a primary material. Fly ash geopolymers also have a lower water demand compared to portland cement concrete mixtures primarily due to the greater volume of fly ash present in the geopolymer mixture (Duxson et al. 2007).

2.3.3 Chemical and Mechanical Properties

In most cases, the chemical composition of the aluminosilicate precursor and the concentration and composition of the activating solution are responsible for the performance of the geopolymer (Sofi et al. 2007). Given the correct mixture design, raw materials, and curing methods, geopolymers show better mechanical performance and

chemical resistance than portland cement concrete mixtures (Duxson et al. May 2007; Duxson et al. 2007; Sofi et al. 2007).

High early strength gain is observed in most heat-cured geopolymers as well as continued compressive strength gain after the curing period, due to the continuation of the polymerization reaction (Duxson et al. 2007; Sofi et al. 2007). The compressive strength of portland cement concrete is greatly dependent on its application. However, typical compressive strength values for normal portland cement concrete range from 3000 psi to 6000 psi (20-40 MPa). Studies have found that geopolymers can exhibit compressive strengths ranging from 30-60 MPa at 28 days (Jang, Lee, Lee 2014; Sofi et al. 2007). The tensile strength of geopolymer concrete has also been found to be consistent with values that can be expected by portland cement concrete, while flexural strength often exceeds expected values (Sofi et al. 2007). Some geopolymers have also shown good acid and fire resistance and are resistant to chloride penetration (Duxson et al. May 2007; Duxson et al. 2007; Sofi et al. 2007).

One property that could cause problems for some engineering applications is the setting time of geopolymers. They can harden in a matter of minutes at ambient temperatures depending on the mixture proportions (Fernández-Jiménez, Palomo, Criado 2005; Sofi et al. 2007), compared to hours for portland cement concrete. However, geopolymers that set quickly have not shown to deteriorate in performance, and may actually gain strength in harsh conditions (Duxson et al. 2007).

2.3.4 Obstacles

There are many obstacles that stand in the way of the widespread market adoption of geopolymer concrete. One of the reasons geopolymers are not in common use is due to variability in performance due to the wide variety of chemical composition among waste materials commonly used. Fly ash is a good example of this because its composition varies based on the impurities found in the coal, as well as the burning conditions at the plant. A source of fly ash in the western U.S. will likely have a different chemical composition than a fly ash source in the eastern part of the country. Likewise, glass composition varies based on the type of recycled glass source. Recycled soda-lime glass (most common) has a different composition compared to recycled fiberglass. Portland cement, on the other hand, is much more consistent as it is produced in a controlled environment and subject to compositional standards (ASTM C150 2005).

Prescriptive regulations and standards have also delayed geopolymer technology from gaining acceptance within the concrete industry. A geopolymer may perform as required, but cannot be used due to prescriptive standards requiring ‘minimum cement content’ as a passing criteria. In some cases, geopolymers meet performance-based specifications such as ASTM C1157 (ASTM C1157 2008), but there is still a lot of work that needs to be done before building codes and other standards are updated to the point of widely accepting these new materials (Duxson et al. 2007).

Another hurdle, from a practical standpoint, is the fact that low-calcium geopolymers require a hydrothermal curing process (typically 40-80°C) to achieve the desired mechanical and durability performance, whereas the curing requirements for portland cement concrete are easily accomplished under ambient conditions. This means moisture and elevated temperatures are required to achieve high early strength. This obstacle limits geopolymer concrete to applications such as precast members.

Concrete mixture designs have an abundance of historical data that reflects what each ingredient offers in terms of performance and workability. For example, water content is directly related to compressive strength and hydration of portland cement concrete. However, unlike portland cement which has been around for hundreds of years, there is little long-term data available to develop a good understanding of how different parameters affect the long-term durability and performance of geopolymers, such as the effects of the water-solids ratio. Understanding the role water plays in geopolymer performance and production could lead to a more consistent mixture design, similar to portland cement concrete mixture designs.

Due to these obstacles and others, geopolymer technology has yet to establish itself as a reliable environmental solution for the concrete industry (Duxson et al. 2007). However, with the environmental and health risks associated with the production of portland cement, an alternative is necessary (Shi, Jiménez, Palomo 2011). In order to reach its full potential, the chemistry and mechanisms of geopolymerization must be better understood,

which begins with an in depth understanding of how they are produced (Duxson et al. 2007).

2.4 Geopolymer Production

2.4.1 Materials

The chemical composition of materials used to produce geopolymers can vary greatly from that of portland cement and will be discussed individually in later sections. While materials such as fly ash and slag can be added to portland cement as supplementary cementitious materials to improve mechanical properties and durability performance, they are usually only present as a supplement and do not act as the primary cementing material. Also, ordinary portland cement concrete is hydrated by adding water to the mixture. However, to produce geopolymers, an activating solution is required for the geopolymerization reaction to take place. The chemical composition of the aluminosilicate sources and the activating solutions are important in order to understand geopolymer production and to compare mechanical properties of the different mixtures.

Geopolymer precursors range from high-calcium aluminosilicates, such as ground granulated blast furnace slag and Class C fly ash, to low-calcium aluminosilicates, like recycled waste glass, metakaolin, and Class F fly ash. The amount of calcium in the mixture is important, as it leads to differences in the types of phases that can form. The phase separation and coexistence of calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) gels are an important topic of interest. In very

alkaline mixtures, calcium plays less of a role because the higher alkalinity forms hydroxide precipitates rather than the desired polymerized gels (Provis and vanDeventer 2009). Crystallinity of aluminosilicate sources is also very important. Amorphous sources produce higher strength geopolymers compared to crystalline sources because sources that are amorphous are easier to break down and therefore able to react better with the activating solution (discussed in Section 2.4.2.1).

2.4.2 Reaction Mechanisms

The reactions that take place during geopolymer production differ significantly from the hydration reactions that take place between portland cement and water. The reaction mechanisms involved in the production of geopolymers are basically the same for any of the low-calcium aluminosilicate sources mentioned above. This means that even though the rate at which the mechanisms occur are dependent on the physical properties and chemical compositions of the materials, the mechanisms controlling the general process of activation are not dependent on the material (Fernández-Jiménez, Palomo, Criado 2005).

One of the first accepted models used to describe geopolymer reaction mechanisms was the Glukhovsky Model. In the 1950s, Glukhovsky described the process in three stages where the aluminosilicate source is first broken down in a highly concentrated alkali solution, then the individual alumina and silica particles accumulate to form a gel, and finally the gel crystallizes to create a geopolymer (Duxson et al. May 2007; Shi, Jiménez,

Palomo 2011). The current consensus on how the reaction mechanisms work is more specific, shown in Figure 2.6 and discussed in the following sections.

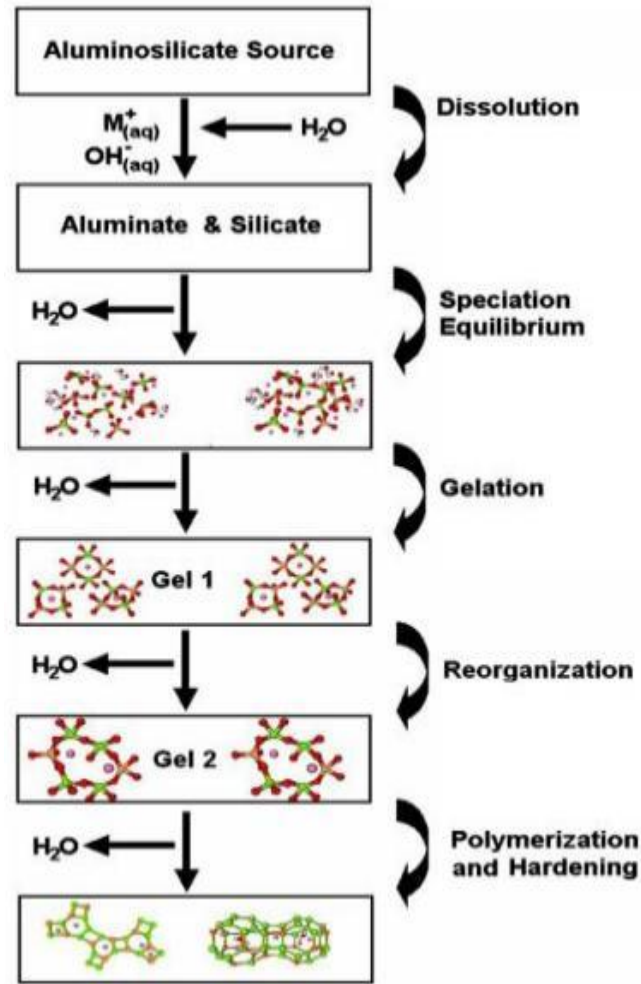


Figure 2.6: Simplified model for geopolymer reaction mechanism (Duxson et al. May 2007).

2.4.2.1 Dissolution

Alkali activation first involves the dissolution of the aluminosilicate source into individual alumina and silica ions. This begins the instant the aluminosilicate source comes in contact with the activating solution. In the case of fly ash, the activating

solution dissolves the outer shells of the larger spheres, which uncovers smaller spheres that may be trapped inside the larger ones. The dissolution rate is dependent on the pH of the activating solution and the crystallinity of the aluminosilicate source (Fernández-Jiménez, Palomo, Criado 2005). Dissolution may not occur at all if the activating solution is too diluted, which can cause problems with mechanical performance due to unreacted particles. An activating solution with a higher pH and a more amorphous aluminosilicate source results in a faster dissolution rate, leading to a supersaturated aluminosilicate solution (Duxson et al. May 2007).

2.4.2.2 Polymerization

Once a supersaturated solution is reached, alumina and silica monomers begin to polymerize together to form larger molecules. These larger molecules form a gel containing chains and rings of tetrahedral silica and alumina molecules (N-A-S-H gel). This gel is the main reaction product of alkali activation. The reaction rate of the process can be slowed down if the gel covers any unreacted particles, in which case diffusion becomes the main reaction mechanism. The uniformity of the gel is dependent on the particle size and homogeneity of the aluminosilicate source and the composition of the activating solution (Fernández-Jiménez, Palomo, Criado 2005).

2.4.2.3 Growth

As the reactions continue, the N-A-S-H gel produced during the polymerization phase of alkali activation continues to reorganize itself, grow and crystallize. This stage can take a long time depending on the ratio of activating solution to aluminosilicate. The rate at

which the polymerization reaction occurs affects the crystallinity of the geopolymer (Fernández-Jiménez, Palomo, Criado 2005). While geopolymers are not recognized as crystalline structures, nanocrystals surrounded by amorphous aluminosilicate gel has been observed in electron diffraction studies (Provis, Lukey, Van Deventer, Jannie S. J. 2005). Additionally, the amount of time and the temperature at which curing occurs greatly impacts the development of the gel. It has been well documented that the rate of the reactions increase as temperature increases, usually leading to enhanced mechanical strength properties (Duxson et al. May 2007).

The N-A-S-H gel is the desired reaction product in geopolymer production. If enough calcium exists in the aluminosilicate blend or activating solution, C-A-S-H and C-S-H products can also both exist. Research shows that C-S-H and N-A-S-H gels are compatible in alkali-activated lime and metakaolin mixtures (Shi, Jiménez, Palomo 2011). If too much moisture exists within the geopolymer or the activating solution is too diluted, crystalline zeolites can potentially form. Zeolites are not a desirable phase in geopolymers and are discussed more in 2.5.2.

2.4.3 Effect of Activator Composition on Geopolymerization

The activating solution plays a very large role in the production of the geopolymer, and is usually an alkali-hydroxide or alkali-silicate solution. Sodium hydroxide (NaOH) is the most common hydroxide solution used to produce geopolymers due to low cost and availability. The activating solution is responsible for dissolving the aluminosilicate source and breaking it up into individual silica and alumina ions. The rate at which

dissolution occurs is dependent on the concentration of the NaOH solution. If the concentration is too low, dissolution will not occur and the desired products will not form. However, if the concentration is too high, secondary dissolution of the reaction products can occur. Generally, as molarity increases, compressive strength also increases (Budh and Warhade 2014).

Sodium silicate is another activating solution commonly used to make geopolymers. The major difference between sodium silicate and sodium hydroxide is that sodium silicate contains pre-dissolved silica. This causes differences in the viscosity and heat of dissolution (Provis and vanDeventer 2009). Including pre-dissolved silica in the activator reduces the time it takes for the mixture to reach supersaturation, changing the reaction rates of the geopolymer. Dissolution still occurs; however, polymerization ensues much faster due to the sodium silicate molecules essentially being locations for the alumina and silica monomers to attach (Criado et al. 2007).

2.4.4 Effect of Elemental Oxide Stoichiometry on Reaction Mechanisms

The exact composition of the aluminosilicate precursor also plays a large role in how reactions occur and ultimately how the geopolymer performs. There are two main stoichiometric ratios of interest when designing a geopolymer mixture, the molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, often abbreviated as Si/Al and Na/Al.

Duxson et al. suggest that in order for geopolymer technology to be used as a sustainable alternative to portland cement, these molar ratios must be relatively contained due to

strength, thermal durability, and the tendency to dissolve in water (Duxson et al. 2007). When silica and sodium are mixed together without alumina, the mixture can become water soluble. Adding alumina to the mixture stabilizes the silica bonds. However, chemically, the sodium content must match alumina content to stabilize the alumina. This means that the ratio of Na/Al must be near unity for mechanical and durability performance (Duxson et al. 2007). If the Na/Al ratio is too high, sodium carbonates can form on the surface of the geopolymer (see Figure 2.7). However, if the Na/Al ratio is too low the set time, microstructure, and overall mechanical performance may be negatively affected.



Figure 2.7: Sodium carbonate forming on outside of preliminary geopolymer mixtures, demonstrating what happens when the Na/Al ratio is too high.

The Si/Al ratio is dependent on the composition of the aluminosilicate materials used, but a Si/Al ratio of 1-5 is generally sought after. Some aluminosilicates, such as waste glass,

do not contain much alumina in relation to silica which results in a higher than normal Si/Al; this can be decreased by blending in other higher-Al materials such as metakaolin or fly ash (Christiansen 2013).

2.4.5 Comparison of Geopolymer and Portland Cement

Two of the biggest differences between geopolymer production and the production of portland cement concrete are the materials involved and the curing requirements.

Geopolymers can be made using high volumes of industrial waste byproducts and other waste materials, while limestone and other raw materials are used to create portland cement. Since raw calcium carbonate is not included in geopolymer production, it results in a much lower carbon footprint (Duxson et al. 2007). Due to significantly less calcium being present in geopolymers, the strength of the resulting concrete does not depend on the formation of calcium-silica-hydrate (C-S-H). Instead, geopolymers rely on a sodium-alumina-silica-hydrate (N-A-S-H) matrix for strength (Sofi et al. 2007). A quick comparison of ordinary portland cement concrete and geopolymers is shown in Table 2.5.

Table 2.5: Comparison of portland cement concrete and geopolymer concrete.

Variable	Portland Cement Concrete	Geopolymer Concrete
Raw Materials	Limestone, Clay, Gypsum	Fly Ash, Glass, Metakaolin
Calcination Process	Yes	No
Primary Elements	Ca, Si	Si, Al, Na
Curing	Wet, Ambient Cure	Wet, Heat Cure
Activator	Water	Alkali Solution
Desired Phase	C-S-H Gel	N-A-S-H Gel

2.5 The Role of Water in Geopolymers

In geopolymer production, water primarily acts as the reaction medium for geopolymerization reactions to take place (Duxson et al. May 2007; Shi, Jiménez, Palomo 2011). During the polymerization process, water is consumed through a dissolution reaction and then expelled back into the mixture through a condensation reaction (Duxson et al. May 2007; Shi, Jiménez, Palomo 2011). These reactions continue until the silica and alumina ions are securely bonded together in a bi-phasic sodium-aluminosilicate gel, commonly referred to as N-A-S-H (Shi, Jiménez, Palomo 2011). Water in geopolymers is not chemically bound to the reaction products to the extent that it is in portland cement concrete. Instead, most of the water exists beside the reaction products, creating nano-pores within the geopolymer matrix. Some studies have shown the nano-pores created by the expelled water improve freeze-thaw durability (Provis and vanDeventer 2009).

2.5.1 Water-Solids Ratio

The water-solids ratio in geopolymers is very similar to the water-cement ratio in portland cement concrete. The water-solids ratio is defined as the ratio of the total mass of water (water in activating solution and additional water for workability) to the total mass of geopolymer solids (aluminosilicate source(s) and solids in activating solution). Just as in portland cement, there is a minimum amount of water required for the reaction products to form. However, because the chemical composition of the materials used to make geopolymers varies so much from mixture to mixture, there is not a well-defined, minimum water-solids ratio. If the activator concentration is high enough, the presence of more water in the mixture will accelerate the dissolution process. However, the presence of more water during the condensation/polymerization phase, where water is released, will slow the reactions (Zuhua et al. 2009). Therefore, there must be a balance where there is enough water in the mixture for dissolution to occur, but not so much that the activating solution becomes diluted and halts the polymerization process.

There has been little research conducted to determine the effects of the water-solids ratio on mechanical properties of geopolymers (Provis and vanDeventer 2009). Most geopolymer research focuses on reaction mechanisms and how varying aluminosilicate compositions or activating solutions affect various properties. Whether they use one aluminosilicate blend and one water-solids ratio to compare a different activator or mixture design ratio, or different aluminosilicate blends and different water-solids ratios to compare properties (Jang, Lee, Lee 2014; Sofi et al. 2007; Steveson and Sagoe-

Crentsil 2005), it is very difficult to directly compare properties between mixture compositions using different water-solids ratios if the water-solids ratio affects the properties of interest.

2.5.2 Zeolites

Zeolites, like those shown in Figure 2.8, are naturally occurring, crystalline aluminosilicate phases that form when a combination of silica and alumina are mixed with a low molarity base in an aqueous solution and exposed to heat over time. The type of zeolite created is dependent on the ratio of the elements included (Davidovits 2008). Synthetic zeolites are often used in water purification and softening applications, and in chemistry to separate and trap molecules for examination.

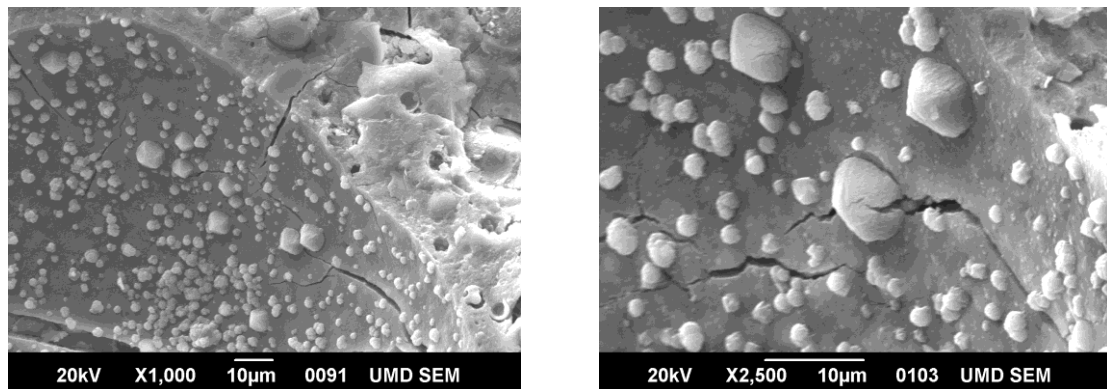


Figure 2.8: Zeolites observed during microstructural analysis.

During the geopolymer production process, there is a possibility for zeolites to form. The presence of zeolites in geopolymer mixtures generally means there is an excess amount

of water. Zeolites don't provide any strength and therefore are not a desired product in geopolymers (Provis and vanDeventer 2009).

2.5.3 Curing Requirements

Similar to curing portland cement concrete, curing geopolymers also requires water. Studies have shown that curing geopolymers in ambient conditions can result in large amounts of shrinkage, while curing them under conditions with adequate heat and moisture show a slight expansion of the material (Zuhua et al. 2009). The ultimate compressive strength and the rate at which that strength is developed are greatly dependent on the curing method. Curing geopolymers in a hydrothermal condition (heat and moisture) accelerates dissolution reactions, which also enhances other geopolymerization reactions (polymerization and growth phases). Therefore adding heat and moisture to the curing process increases the compressive strength at early ages. However, if cured with too much moisture, the polymerization phase could be slowed down, causing low compressive strengths. Zeolites can also form in the presence of too much heat and moisture. The amount of heat depends on the composition of the aluminosilicate sources used (i.e., higher calcium content requires more heat). However, various researchers have used curing temperatures ranging from 20-80°C and around 90% relative humidity (Zuhua et al. 2009).

2.6 Literature Review Summary

Portland cement concrete is the most widely used infrastructure material in the world. Portland cement production alone accounts for 5% of the global CO₂ emissions and is the

third largest source of carbon emissions in the United States. With these environmental concerns involving cement production, the investigation into alternative binders is necessary.

There are many advantages to using portland cement and portland cement concrete, and production and proportioning mixture designs are well understood based on historical performance data. Geopolymers, on the other hand, are a relatively new infrastructure material compared to portland cement. They are made when an aluminosilicate source, such as waste glass or fly ash, is mixed with an alkali activator, such as sodium hydroxide. The production of geopolymers does not require a calcination process, which is responsible for half of the carbon emitted during portland cement production. This drastically cuts carbon emissions, making geopolymers more sustainable. Production of geopolymers relies on an alkali activator to break down the aluminosilicate source so that polymerization reactions can take place between the individual silica and alumina monomers. The quality and rate at which these reactions take place is dependent on the concentration of the alkali activator as well as the water-solids ratio. Given quality material and the correct mixture proportions, geopolymers can achieve better durability and mechanical properties compared to portland cement, while also being much more sustainable.

One thing that is understood very well about portland cement is the role water plays in hydration, curing, and performance. Water is chemically bound within the hydration

products and is required for concrete to hydrate properly after the initial reactions occur. It is also a well-known fact that the water-cement ratio is a key component of mixture design, as it affects strength and durability properties. As the water-cement ratio increases, compressive strength and durability decrease and vice versa. However, the role of water in geopolymers isn't understood as well.

Much of the research examining geopolymer technology has focused on specific mechanical properties, reaction mechanisms, and how using materials of varying compositions affects physical and mechanical properties. There has been limited research on the effects of the water-solids ratio (w/s) on geopolymer production and performance. Whether or not the water-solids ratio in geopolymers has the same effect on mechanical properties as the water-cement ratio in portland cement concrete is relatively unknown due to a lack of historical data and research. Understanding the water-solids ratio in geopolymers is important for designing mixtures easily and can help in identifying the necessity of admixtures. Therefore, the research described in this paper focuses on how the water-solids ratio affects the compressive strength and degree of reaction of fly ash-waste glass-based geopolymers.

Many studies either use one aluminosilicate blend and one water-solids ratio to compare a different activator or mixture design ratio, or they use different aluminosilicate blends and different water-solids ratios to compare properties and performance (Jang, Lee, Lee 2014; Sofi et al. 2007; Steveson and Sagoe-Crentsil 2005). However, it is very difficult to

directly compare properties between mixture compositions using different water-solids ratios. In other words, the water-solids ratio could be what affects the properties of interest. Therefore, this research also tries to answer the question of whether or not direct comparisons can be made to mixtures using different aluminosilicate blends and different water-solids ratios.

3 Materials and Experimental Methods

3.1 Experimental Plan

Five different geopolymer mixtures composed of varying amounts of waste glass and Class F fly ash were investigated. Three water-solids ratios were examined for each of the mixture compositions. Each set of samples was tested for compressive strength, degree of reaction, and examined under a scanning electron microscope (SEM) to discover any trends from changing the water-solids ratio. The mixture compositions used are shown in Table 3.1. Designations for the mixture IDs are the percentage of the aluminosilicate used in the blend (G = glass, FA = fly ash). For example, 75G25FA stands for a mixture using 75% glass and 25% fly ash.

Table 3.1: Mixture compositions used to evaluate the effect of the water-solids ratio.

Mixture ID	Glass (% mass of total aluminosilicate)	Fly Ash (% mass of total aluminosilicate)	Water-Solids Ratio Range
100G	100	0	0.450-0.500
75G25FA	75	25	0.400-0.450
50G50FA	50	50	0.375-0.425
25G75FA	25	75	0.350-0.400
100FA	0	100	0.350-0.400

3.1.1 Phase I – Compressive Strength

The first phase of this research examined the effect of the water-solids ratio on the compressive strength of the geopolymer mortars. The influence of the water-solids ratio on compressive strength was expected to be similar to the behavior exhibited by portland cement. A w/s ratio that was too high was expected to result in lower compressive

strength due to diluting the activating solution, and a w/s that was too low was also expected to result in a low compressive strength due to less dissolution occurring. In an effort to see these trends, three water-solids ratios were selected for each mixture based on consistency and workability. Compressive strength data was collected by breaking test cylinders at 1, 7, 28, and 56 days. The testing procedure used for compressive strength is covered in 3.4.1.

3.1.2 Phase II – Degree of Reaction

Similar to investigating the extent to which portland cement hydrates, the second phase of this research focused on the degree to which the aluminosilicate sources dissolved during geopolymerization. Degree of reaction tests (discussed in 3.4.2) were conducted on geopolymer paste samples of each mixture after curing for seven days. A curing period of seven days was selected based on compressive strength data from Phase I. The degree of reaction was expected to correlate with compressive strength. In other words, if a particular geopolymer mortar exhibited high compressive strength, it was expected that the corresponding geopolymer paste would have a high degree of reaction.

3.1.3 Phase III – Microstructural Analysis

In the third and final stage of this research, the microstructure of the geopolymer mortars was examined under a scanning electron microscope (SEM). The SEM investigation focused on locating unreacted particles, zeolites, and observing the porosity of the microstructure. The data collected in Phase III was compared to findings in Phases I and II. Information about the SEM and imaging settings can be found in Section 3.4.3. It was

expected that more unreacted particles and more zeolites would be present in mixtures with higher water-solids ratios.

3.2 *Materials*

3.2.1 Waste Glass

This research used a pre-processed (washed, ground) waste glass from fiberglass manufacturing, shown in Figure 3.1.

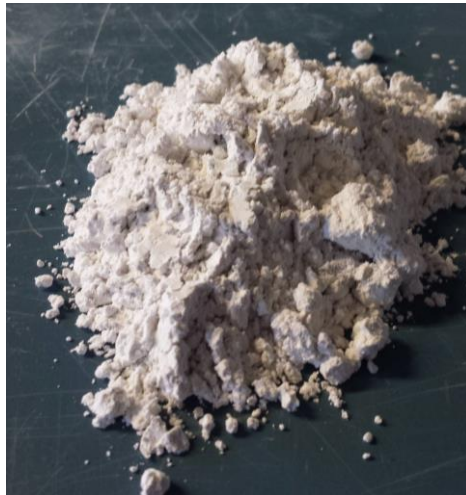


Figure 3.1: Ground glass powder used in research.

The average particle size (d_{50}) of the glass used in this research was $3.32\ \mu\text{m}$ and d_{90} was $11.64\ \mu\text{m}$ (data courtesy of UMD CE MS student Kyrstyn Haapala). The particle size distribution is shown in Figure 3.2.

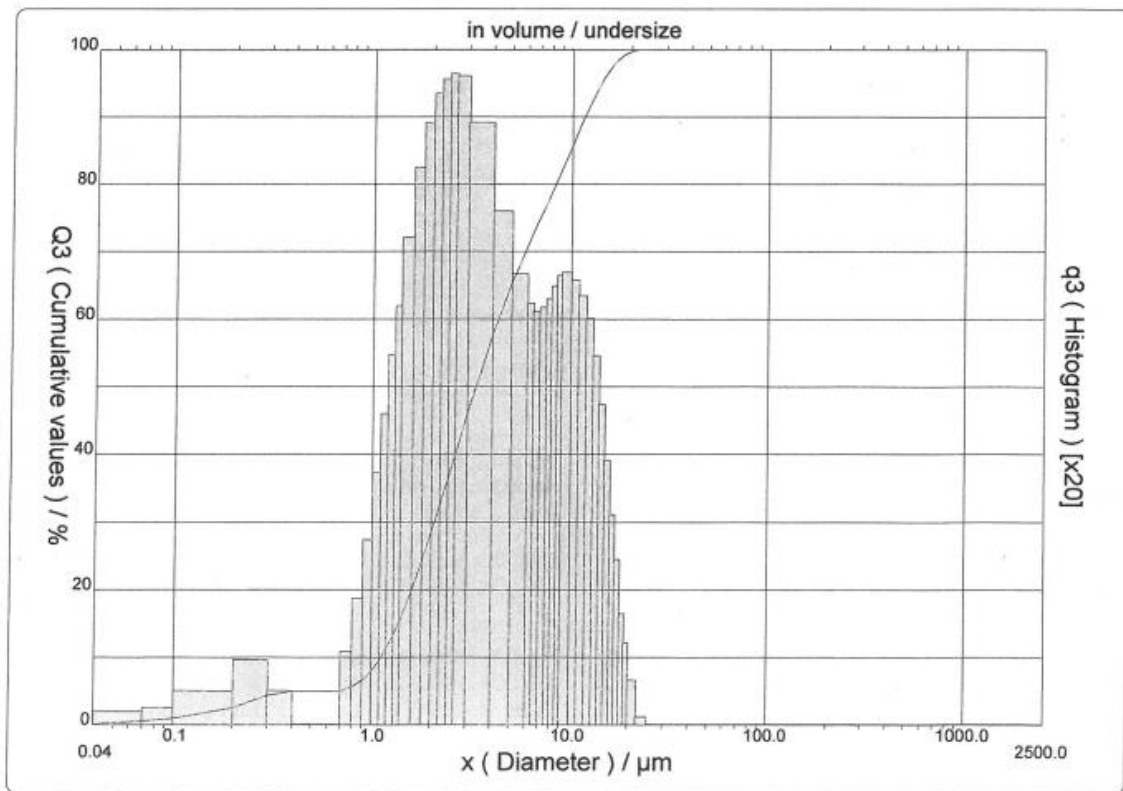


Figure 3.2: Particle size distribution graph of waste glass used.

The chemical composition of the glass is given in weight percent oxides and was determined using x-ray fluorescence (XRF) analysis conducted by Wyoming Analytical Laboratories, Inc. and is shown in Table 3.2 along with the chemical composition of typical soda-lime glass. Typical soda-lime glass accounts for about 90% of all manufactured glass and consists of bottles, glass containers, and windows. The waste glass used in this research, as shown in Table 3.2, does not qualify as typical soda-lime glass, but rather is considered e-glass based on its composition. E-glass has significantly higher amounts of Al_2O_3 and CaO , and significantly lower amounts of SiO_2 and Na_2O than typical soda-lime glass ranges for those oxides.

Table 3.2: Chemical composition of the glass used in this research by weight percent oxide (Wyoming Analytical Laboratories 2014). Typical soda-lime glass content is included for comparison.

Oxide	Glass Used in Research	Typical Soda-Lime Glass
Silicon Dioxide, SiO ₂	60.25	70-75
Aluminum Oxide, Al ₂ O ₃	12.19	0-2
Iron Oxide, Fe ₂ O ₃	0.31	0-0.5
Calcium Oxide, CaO	21.72	8-12
Magnesium Oxide, MgO	3.01	0-5
Sodium Oxide, Na ₂ O	0.87	10-15
Sulfur Trioxide, SO ₃	0.01	0-0.5
Potassium Oxide, K ₂ O	0.08	0-0.5
Phosphorus Pentoxide, P ₂ O ₅	0.04	NA
Titanium Dioxide, TiO ₂	0.89	0-0.10
Moisture Content	0	NA
Loss on Ignition	0.59	NA

3.2.2 Fly Ash

Fly ash is an industrial byproduct from the combustion of coal at coal-fired power plants. Fly ash, shown in Figure 3.3 is known to increase workability and set time, while decreasing water demand in portland cement concrete. Geopolymer mixtures containing fly ash also require less water due to the spherical shape of the ash particles (Provis and vanDeventer 2009).



Figure 3.3: Class F fly ash.

The fly ash used in this research was provided by Arrowhead Concrete, and had an average particle size (d_{50}) of 11.89 μm and d_{90} of 49.01 μm (data courtesy of UMD CE MS student Kyrstyn Haapala). The particle size distribution is shown in Figure 3.4.

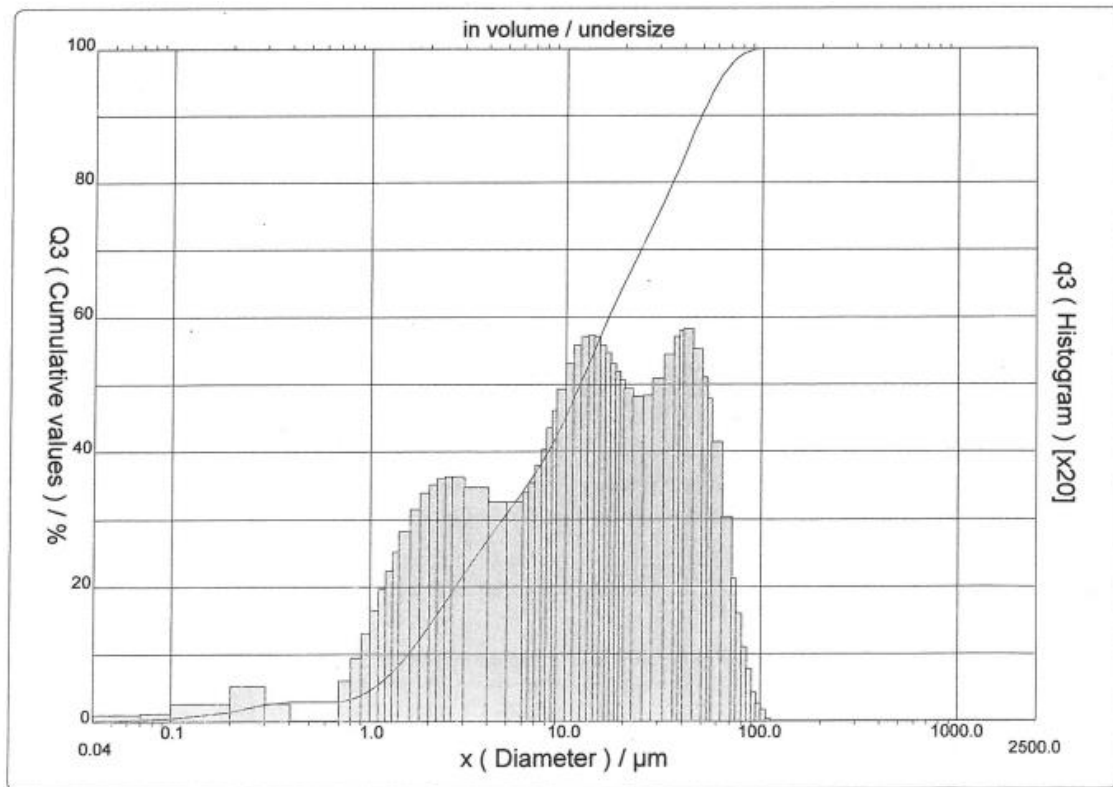


Figure 3.4: Particle size distribution of fly ash used.

The fly ash used in this research, was a low-calcium, Class F fly ash. Table 3.3 displays the chemical composition of the fly ash used in this research.

**Table 3.3: Chemical composition of Class F fly ash used in this research by weight percent oxide
(Wyoming Analytical Laboratories 2014).**

Oxide	Class F Fly Ash
Silicon Dioxide, SiO ₂	51.10
Aluminum Oxide, Al ₂ O ₃	15.61
Iron Oxide, Fe ₂ O ₃	5.73
Calcium Oxide, CaO	15.11
Magnesium Oxide, MgO	4.97
Sodium Oxide, Na ₂ O	2.44
Sulfur Trioxide, SO ₃	0.76
Potassium Oxide, K ₂ O	2.27
Phosphorus Pentoxide, P ₂ O ₅	0.22
Titanium Dioxide, TiO ₂	0.25
Moisture Content	0.06
Loss on Ignition	0.20

To demonstrate the variability in elemental oxide composition between the glass, fly ash and ordinary portland cement, all three are graphed on a ternary diagram shown in Figure 3.5. The oxides of interest were silica (SiO₂), alumina (Al₂O₃), and lime (CaO). Ordinary portland cement is also plotted in the graph for comparison.

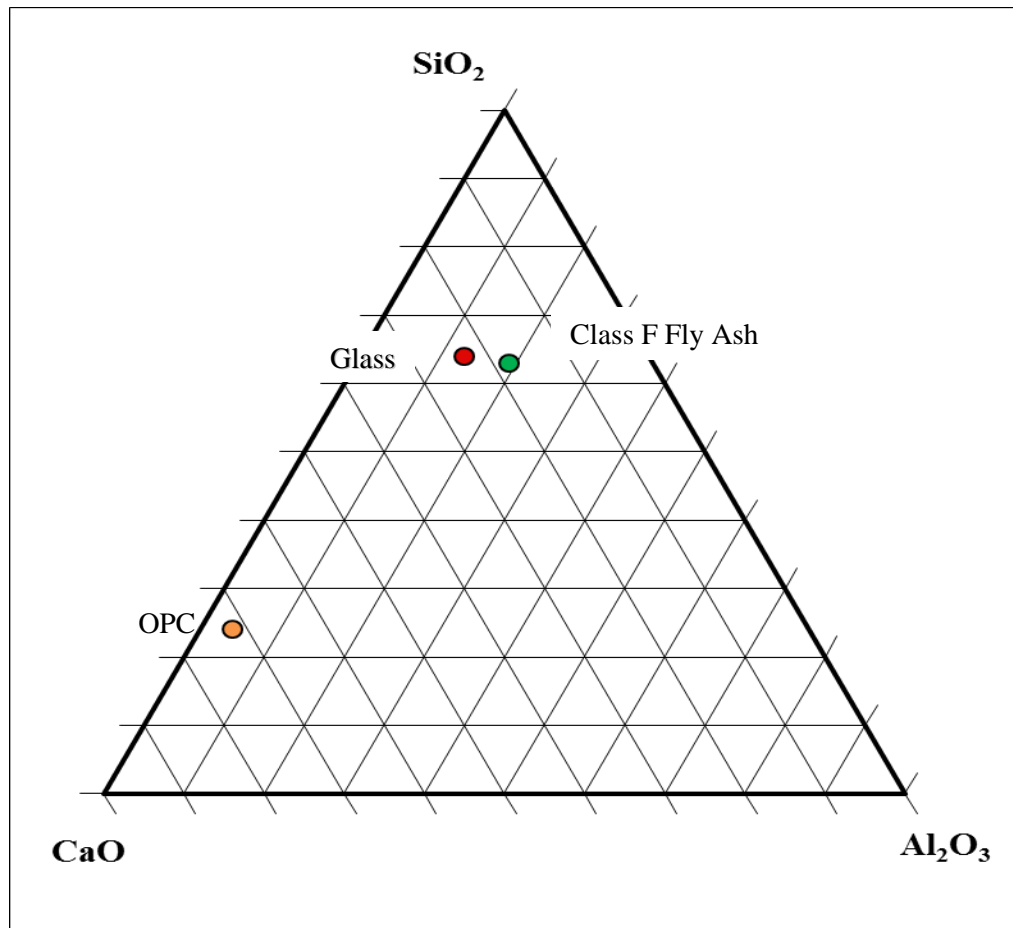


Figure 3.5: Silica, alumina, and calcium oxides in the source materials used in this research (Graham and Midgley 2000)

3.2.3 Sodium Hydroxide

The primary activating solution used in this research was sodium hydroxide, NaOH.

Sodium hydroxide flake was mixed with deionized water at least 24 hours prior to blending with the aluminosilicate in order for it to reach room temperature. The molarity of the sodium hydroxide mixture used in this research stayed constant at 10M, which is similar to other studies where glass or fly ash was used (Christiansen 2013; Rattanasak and Chindaprasirt 2009). NaOH flake, shown in Figure 3.6, and activating solutions in

general are corrosive, so safety measures (gloves, safety glasses, etc.) were used to prevent injury. The chemical composition of the NaOH solution is shown in Table 3.4 along with the other activators used.

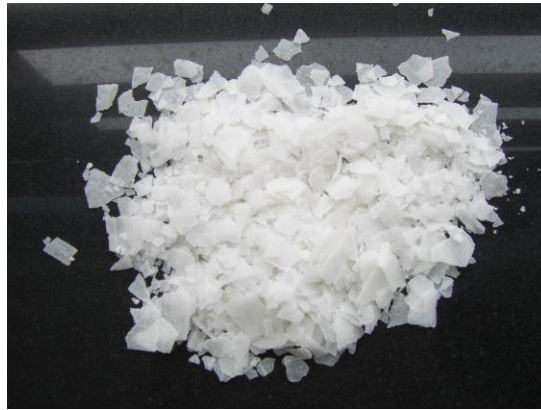


Figure 3.6: NaOH flake used to make alkali-activating solution.

3.2.4 Sodium Silicate

An additional activator was also used where the ratio of sodium silicate (Na_2SiO_3) and NaOH was 1:1. The reason why a NaOH/sodium silicate activator was also used is because less water is required for precursor dissolution due to the pre-dissolved silica in the sodium silicate. This allowed for comparison of the effects of how different activators affect the compressive strength and degree of reaction of geopolymers, while also reducing the water-solids ratio. Many other studies also used a combination of NaOH and sodium silicate as the activator (Fernandez-Jimenez and Palomo 2005; Sofi et al. 2007). Therefore, sodium silicate was also used to try to replicate trends or observations found in other studies. The chemical composition of the sodium silicate solution used in this research is shown in Table 3.4.

Table 3.4: Chemical composition of activator solutions by weight percent oxide.

Oxide	10M NaOH Solution	Na₂SiO₃ Solution	1:1 Activating Solution
H ₂ O	22.53	62.31	42.42
SiO ₂	0.00	28.70	14.35
Na ₂ O	77.48	8.99	43.23

3.2.5 Aggregate

The aggregate used to make mortars was ASTM C778 graded silica sand (ASTM C778 2013). The aggregate/aluminosilicate ratio was 3:1 by mass and remained constant throughout all of the mixtures used.

3.3 Proportioning and Mixing

Five different mixture compositions were examined using sodium hydroxide (NaOH) as the activating solution. In addition, a mixture combining NaOH and sodium silicate (abbreviated with SS) was also tested for each mixture. Sodium silicate was added to see if the activator also had an effect on the water-solids ratio. In each mixture the aggregate/aluminosilicate and activator/aluminosilicate ratios remained constant at 3:1 and 1:2 respectively (Christiansen 2013; Cyr, Idir, Poinot 2012). The aggregate/aluminosilicate ratio of 3:1 is comparable to that of aggregate/cement paste in ordinary portland cement mortar.

Preliminary mixtures were developed to determine an acceptable range of water-solids ratios to be considered. The acceptable w/s range was based on a mixture consistency where the geopolymer would consolidate well, but not to where the mixture was soupy. Fresh properties were evaluated for only three mixture compositions (two using sodium silicate as activator) due to the delayed availability of the testing equipment.

The combinations of aluminosilicates (by mass) and water-solids ratios are shown in Table 3.5. Three water-solids ratios (increments of 0.250) were investigated for mixtures using sodium hydroxide as an activator, and one water-solids ratio was looked at for mixtures using sodium silicate in the activator (which required less water). The lowest allowable water-solids ratio based on the stated mixture constraints was 0.350 for sodium hydroxide mixtures and 0.305 for mixtures activated with the sodium silicate mixture. However, by keeping all variables in the mixtures constant, other than water-solids ratio, the influence water had on compressive strength and degree of reaction was directly comparable between mixtures (See Section 4.6).

Table 3.5: Mixture compositions used to investigate water-solids ratio.

Mixture ID	Glass (% mass of total aluminosilicate)	Fly Ash (% mass of total aluminosilicate)	NaOH Mixtures W/S Ratio Range	SS Mixtures W/S Ratio
100G	100	0	0.450, 0.475, 0.500	0.425
75G25FA	75	25	0.400, 0.425, 0.450	0.400
50G50FA	50	50	0.375, 0.400, 0.425	0.350
25G75FA	25	75	0.350, 0.375, 0.400	0.305
100FA	0	100	0.350, 0.375, 0.400	0.305

An example of the mixture design for the 50% glass, 50% fly ash mixture is shown in Table 3.6. An example of the full mixture design spreadsheet used in this research can be seen in Appendix A.

Table 3.6: Example of 50% glass, 50% fly ash mixture design.

Component	w/NaOH	w/SS
Total Batch Size (g)	6000	6000
Aggregate/Aluminosilicate (mass)	3	3
Activator/Aluminosilicate (mass)	0.5	0.5
SS/NaOH (mass)	0	1
CS-600 Glass (g)	667	667
Class F Fly Ash (g)	667	667
NaOH Solution (g)	667	333
SS Solution (g)	0	333
Aggregate (g)	4000	4000

3.3.1 Mixture Stoichiometry

As discussed in Section 2.4.4, several specific molar ratios are important for the stability of geopolymers in moist environments. An Si/Al ratio between 1:1 and 5:1, and a Na/Al near 1:1 is generally the range where strong and stable geopolymers form. Stoichiometric molar ratios for each mixture are shown in Figure 3.7. Mixtures with the abbreviation “w/SS” used a combination of sodium hydroxide and sodium silicate for the activating solution.

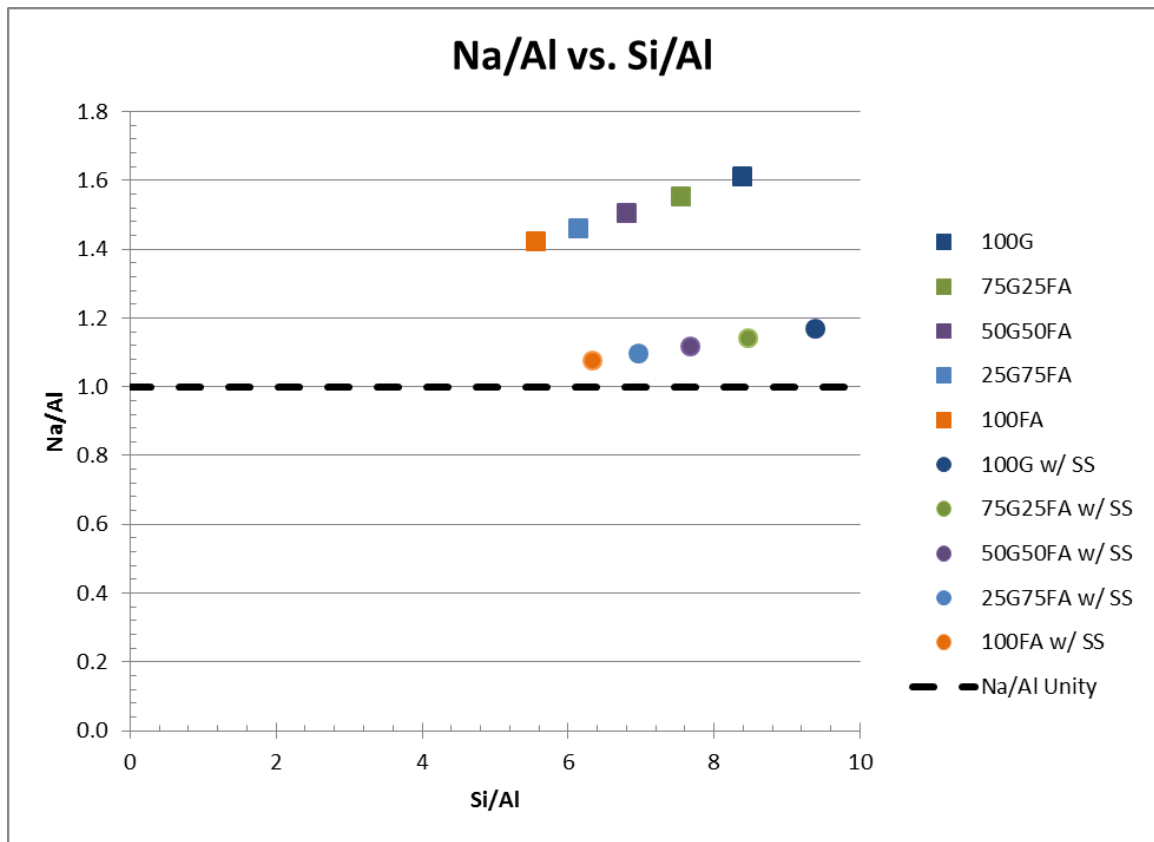


Figure 3.7: Si/Al and Na/Al molar ratios of mortars.

These ratios are slightly higher than those said to make the best performing geopolymer mixtures ($\text{Si/Al} = 5$ and $\text{Na/Al} = 1$) (Duxson et al. 2007). Two things to note are 1) that as fly ash content increased from 0% (100G mixture) to 100% (100FA mixture), the Na/Al and Si/Al ratios decreased regardless of the activating solution, and 2) when using sodium silicate in the activating solution, the Na/Al ratio decreased and the Si/Al ratio increased (due to the additional silica). From a mixture design standpoint, this could be very important when proportioning geopolymer mixtures to achieve greater stability and strength. These ratios will be reviewed further in the results section of this research (Section 4).

3.3.2 Mortar Mixing

Mortar samples were selected over concrete samples in order to eliminate additional variables involved with concrete testing (i.e., aggregate moisture). Using oven dry silica sand eliminated the need to test for absorption and moisture of the fine aggregate. Mortar mixing and curing followed a modified ASTM C192 procedure (ASTM C192 2012).

All of the mortars were mixed using a Hobart mixer. Similar to the procedure used to mix portland cement mortars, the dry ingredients (fly ash and glass) were first blended together for 3 minutes. Then the activating solution was added slowly over 1 minute, and the paste was allowed to mix for another 3 minutes, this is shown in Figure 3.8. The appropriate amount of water to achieve the desired water-solids ratio was added slowly over this time. Once the paste was thoroughly mixed, silica sand was added over a period of 2 minutes. The mixture was then left to mix for an additional 6 minutes, bringing the total mixing time to 15 minutes.



Figure 3.8: Geopolymer mortar mixing.

At fifteen minutes, the mortar was placed in 2" x 4" cylinders in two layers (each layer was rodded), and then set on a vibration table for 10 seconds. Fresh properties were not tested for some of the early mixtures based on the availability of equipment (mixing started prior to arrival of equipment). However, once equipment arrived, flow and fresh unit weight was measured. The cylinders were cured in an oven at 80°C for 24 ± 2 hours based on other studies (Zuhua et al. 2009). Upon completion of the heat cure, the cylinders were demolded and placed in a controlled environmental chamber set at 23°C and 90% relative humidity until the testing date.

3.3.3 Paste Mixing

Due to the small amount of paste required for the degree of reaction tests, paste samples were mixed by hand. Therefore, a slightly different and shorter mixing procedure was used. The dry ingredients were blended together for 3 minutes to produce a homogeneous mixture. The activating solution was then added to the mixture. Due to the difficulty of

mixing and adding the activating solution at the same time, the activating solution was added quickly and mixing immediately resumed for another 3 minutes. The appropriate amount of water to achieve the desired water-solids ration was then added. Once mixing was complete, the paste was put in a small plastic bag, sealed, and placed in an oven at 80°C for 24 ± 2 hours. Upon completion of the heat cure, the samples were placed in a controlled environmental chamber set at 23°C and 90% relative humidity until the testing date.

3.4 Experimental Procedures

3.4.1 Compressive Strength

The compressive strength of the 2x4 mortar cylinders used in this research was measured according to a modified ASTM C39 (ASTM C39 2012) procedure using the Humboldt compressive strength testing machine shown in Figure 3.9. The modification is that this research tested geopolymer mortar and not concrete. The maximum capacity of the machine is 300,000 pounds and the specimens were loaded at a rate between 88-132 lb/s.



Figure 3.9: Humboldt compressive strength testing machine.

Compressive strength was measured at 1, 7, 28, and 56 days in order to create a sufficient strength development curve. Each data point represents the average of three tests.

Specimen lengths, diameters, and weights were recorded prior to compressive strength testing. If test cylinders were not level on the tops and/or bottoms, the cylinder was cut to create a level surface and reductions were applied per ASTM C39 if required (ASTM C39 2012).

3.4.2 Degree of Reaction

The degree of reaction of a geopolymer is a measure of the extent to which dissolution has occurred. A known mass of paste is ground up and mixed with dilute HCl. The HCl dissolves away the geopolymer phases that have formed, leaving behind unreacted fly ash or glass, which can be weighed and a degree of reaction reported. The tests were

conducted on paste samples at seven days for each mixture, at every water-solids ratio to determine the degree to which the aluminosilicate blends dissolved in the activating solution. Each data point represents the average of three tests. The procedure for the degree of reaction test is as follows:

1. Grind paste samples into a fine powder using mortar and pestle.
2. Add approximately 1 gram (m_i) of powdered paste to 200 mL of (1:20) hydrochloric acid (HCl) solution and mix on a magnetic stir plate for 3 hours.
3. Using ashless filter paper, a Buchner funnel, and vacuum pump, filter the resulting solution and capture the undissolved solid particles on the filter paper (see Figure 3.10).



Figure 3.10: Degree of reaction test setup.

4. Record the mass of an empty crucible (m_c) before placing the used filter paper into the crucible.

5. Place the crucibles containing the filter paper in a muffle furnace at 1000°C until the ashless filter paper burns off (minimum of 24 hours).
6. Record the mass of the crucible and its remaining contents (m_f) and calculate the degree of reaction (α) using the following equation:

$$\alpha = \left(1 - \frac{(m_f - m_c)}{m_i} \right) \times 100 \quad (\text{Eq. 1})$$

A higher degree of reaction, α , means a more complete reaction took place during the dissolution process.

3.4.3 Microstructural Characterization

The microstructure of compressive strength samples that were broken at seven days was examined using a JEOL JSM-6490LV scanning electron microscope (SEM), shown in Figure 3.11. While the mortars examined were tested for compressive strength at seven days, the actual age of the samples during microstructural analysis was over 100 days. The broken compressive strength samples were sealed in a bag until the day they were examined under the SEM.



Figure 3.11: JEOL JSM-6490LV scanning electron microscope.

Secondary electron imaging was used to investigate the topography of the samples and to identify unreacted particles, zeolites, and general properties of the phases formed. To reduce charging on the sample, the samples were coated in gold. An accelerating voltage of 20 kV and a magnification of 2500X was used in order to compare the microstructure of various samples at a consistent scale. For other images (unreacted particles, zeolites, etc.), a magnification that adequately represented the particle of interest was used.

4 Results and Discussion

Section 4 presents the results from all three phases of research (compressive strength, degree of reaction, and microstructural analysis) for each individual mixture, where differences between each water-solid ratio used is the primary focus of discussion.

Following the presentation of the individual mixture data, discussion on the similarities and differences between the mixtures of varying compositions is provided.

4.1 100% Glass (100G)

4.1.1 100G: Compressive Strength

The compressive strength of the 100% glass mixture did not seem to be greatly affected by a changing water-solids ratios, as shown in Figure 4.1. Of the three water-solids ratios selected, using the NaOH solution as the activator (0.450, 0.475, 0.500), the difference in compressive strength was never more than 700 psi. The mixture containing the least amount of water ($w/s = 0.450$) was the strongest in the group and the mixture containing the most water ($w/s = 0.500$) was the weakest, which was expected. However, with such similar strength curves, it was determined that changing the water-solids ratio, within this range, does not have a major effect on compressive strength.

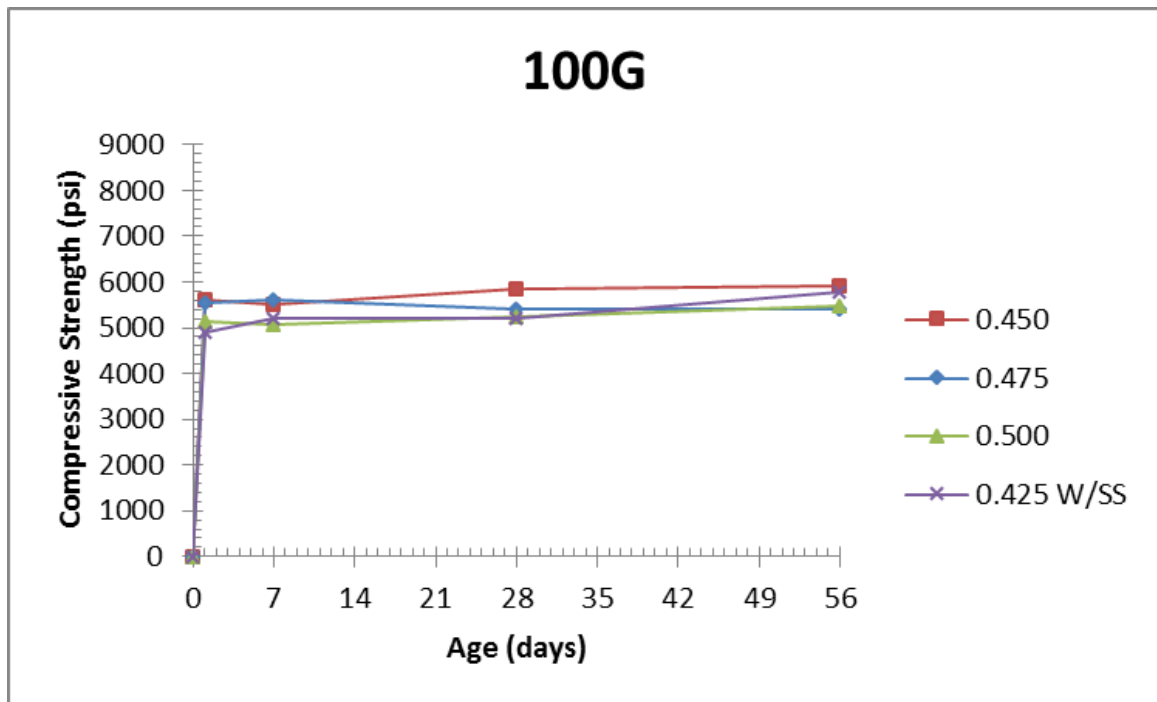


Figure 4.1: Compressive strength curve for 100G mixtures.

The mixture containing sodium silicate in the activating solution exhibited roughly the same strengths as those activated with just sodium hydroxide. However, the strength gain over time (from 1 to 56 days) was much higher for the sodium silicate mixture (nearly 1000 psi) than for the sodium hydroxide mixtures (average of 200 psi strength gain). Individual strength curves for each of the mixtures can be found in Appendix A.

4.1.2 100G: Degree of Reaction

Degree of reaction test results, shown in Table 4.1, correlate well with compressive strength tests in terms of variation between mixtures. On average, a little over 75% of the glass reacted with the activating solution. With a variation of less than one percent

observed between the three water-solids ratios, it can be concluded that the water-solids ratio did not have a significant effect on the degree of reaction in the 100G mixtures.

Table 4.1: Degree of reaction results for the 100G mixtures.

Water-Solids Ratio	Average α (%)	Standard Deviation
0.450	75.7	0.0241
0.475	76.1	0.0117
0.500	76.3	0.0025

4.1.3 100G: Microstructural Analysis

Images of the microstructure in Figure 4.2 show that the microstructures for the 100G mixtures are relatively consistent. While unreacted particles and zeolites were present, an abundance of unreacted particles and zeolites was not observed in any of the three mixtures, indicating adequate water-solids ratios and good reactivity. “Pull-out” sites were identified where it appears unreacted particles may have been before the sample was broken in the $w/s = 0.475$ and $w/s = 0.500$ mixtures. The mixtures with $w/s = 0.475$ and 0.500 had lower strengths than the mixture using $w/s = 0.450$. This could mean the addition of more water decreases the strength of the geopolymer at the interfacial transition zone (ITZ). The ITZ is a region around aggregate particles (or unreacted particles) that generally has a higher water content, and therefore porosity. The higher porosity creates a weak spot and leads to lower strengths. Another consideration is that the surface of the glass particles may be too smooth making it difficult to create a strong bond with the geopolymer product.

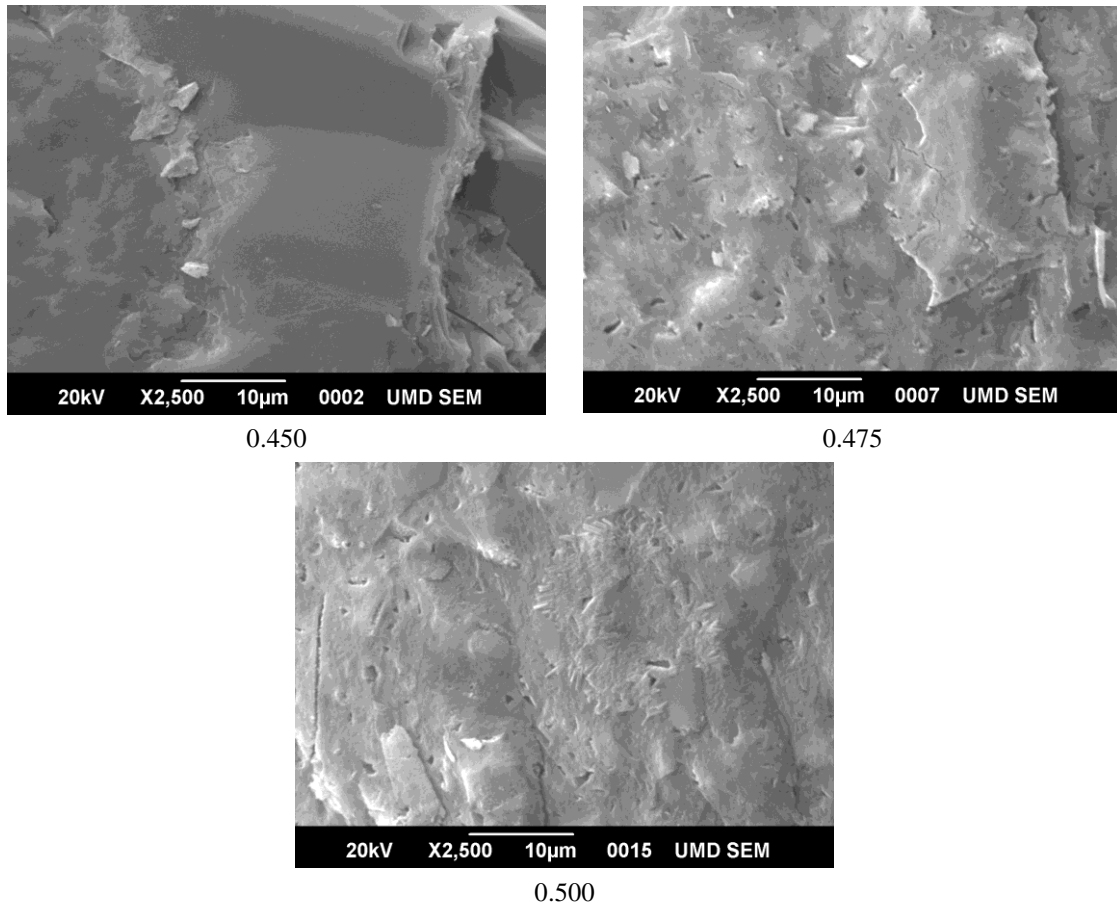


Figure 4.2: Examples of the microstructure of the three 100G mixtures.

4.2 75% Glass, 25% Fly Ash (75G25FA)

4.2.1 75G25FA: Compressive Strength

Fly ash is known to decrease water demand due to the spherical nature of the particles, so the 75G25FA mixtures required less water than the mixtures using just waste glass to reach the same workability. The strengths of the three mixtures using NaOH as an activator were consistently spaced out by approximately 500 psi throughout the 56 days, as shown in Figure 4.3. The driest mixture ($w/s = 0.400$) exhibited strengths around 5500

psi, similar to the 100% waste glass mixtures. The mixture containing the most water (w/s = 0.450) had strengths around 4300 psi at 56 days. It appears that mixtures containing fly ash are more influenced by water content than when just glass is used. The greater sensitivity to water could be due to differences in particle size, particle shape, or atomic structure and composition. This increased sensitivity could also be due to hydrating fly ash particles. Calcium rich phases in fly ash particles can hydrate when exposed to water, creating C-S-H and C-A-S-H reaction products. This is further discussed in Section 5.

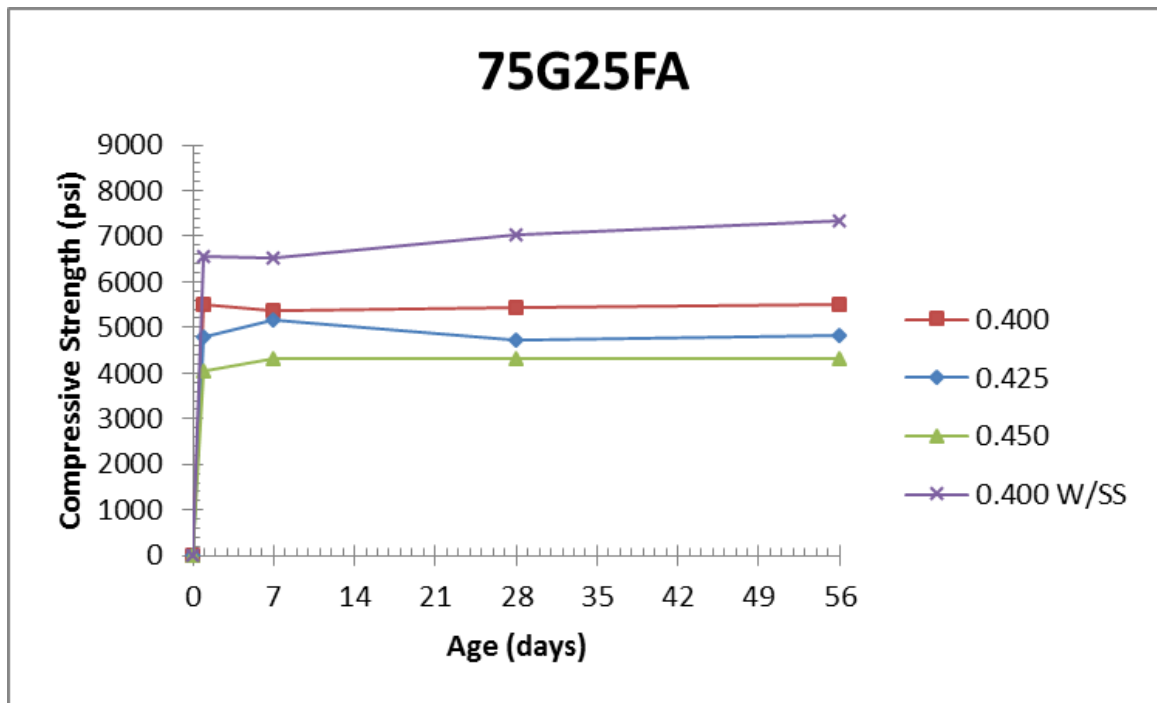


Figure 4.3: Compressive strength curve for 75G25FA mixtures.

The sodium silicate mixture showed strengths that were much higher than the compressive strengths of the sodium hydroxide mixtures (1000-2000 psi). Higher

strengths have been found in fly ash mixtures using sodium silicate in the activating solution versus an activating solution using only sodium hydroxide (Fernandez-Jimenez and Palomo 2005). Fernández-Jiménez and Palomo found that the addition of sodium silicate to the activating solution enhances the polymerization stages of geopolymer production. There was also a considerable amount of strength gained over 56 days in the sodium silicate mixture, whereas the sodium hydroxide mixtures virtually plateaued after 1-7 days. Having said this, in the upcoming mixtures where additional samples were tested at post-56-day tests, significant strength gain was observed. Individual strength curves for each of the mixtures can be seen in Appendix A.

4.2.2 75G25FA: Degree of Reaction

Degree of reaction results shown in Table 4.2 also show a slight influence from the water-solids ratio of the mixture. An average of approximately 71% of the aluminosilicates reacted with the sodium hydroxide solution. It should be noted that the degree of reaction is lowest in the mixture with the lowest water-solids ratio. Intuition would suggest that adding more water would dilute the activating solution during dissolution, slowing the reactions between the aluminosilicate blend and the activating solution. However, the degree of reaction test results seem to suggest otherwise. This could partially be due to the fly ash hydrating. The degree of reaction test procedure assumes the HCl will dissolve any product that is geopolymer product, leaving behind any initial materials such as glass and fly ash particles that did not react. Any C-S-H that would be formed by fly ash hydrating is assumed to dissolve with the geopolymer product.

Table 4.2: Degree of reaction results for 75G25FA mixtures.

Water-Solids Ratio	Average α (%)	Standard Deviation
0.400	69.7	0.0098
0.425	72.4	0.0035
0.450	72.7	0.0045

4.2.3 75G25FA: Microstructural Analysis

Images of the microstructure are shown in Figure 4.4. Zeolites appeared in each of the mixtures, but were more abundant in mixtures where the water-solids ratios were 0.400 and 0.425. An abundance of zeolites (pictures shown in Section 4.9) would usually indicate excess water in the mixture, however, 0.400 was the lowest of the three water-solids ratios used.

“Holes” were identified again, similar to the 100G mixtures, where it appears unreacted glass or fly ash particles or aggregates may have been before the sample was broken, especially in the w/s = 0.450 mixture. The zeolites that were observed were in voids within the geopolymer product. Perhaps, the interfacial transition zone (ITZ) is also a location where zeolites tend to form, and because zeolites are not as strong as the geopolymer product surrounding the ITZ, local failures occur.

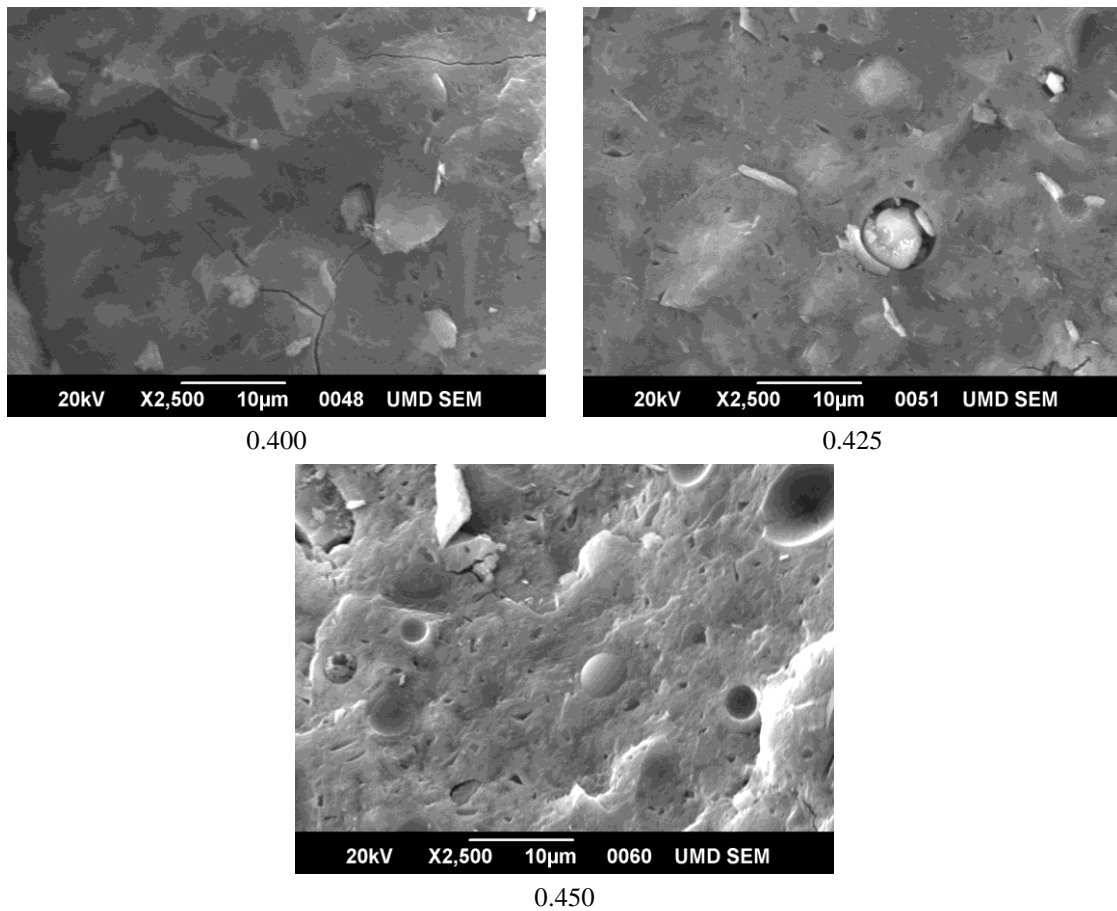


Figure 4.4: Examples of the microstructure of the 75G25FA mixtures.

4.3 50% Glass, 50% Fly Ash (50G50FA)

4.3.1 50G50FA: Compressive Strength

Compressive strengths for the NaOH mixtures ranged from just under 5000 psi (w/s = 0.425) to 5800 psi (w/s = 0.375), as shown in Figure 4.5. Variations between mixtures were relatively consistent throughout the 56-day testing period (higher w/s ratios had lower compressive strengths). Similar to the 75G25FA mixture, it seems that the addition of fly ash increases the impact water has on compressive strength. Again, this could be due to the fact that fly ash has a different particle size, shape, and chemistry, and also has

the ability to hydrate in the presence of water. Prior to adding sand during the mixing procedure, the 50G50FA mixture had the consistency of chocolate milk.

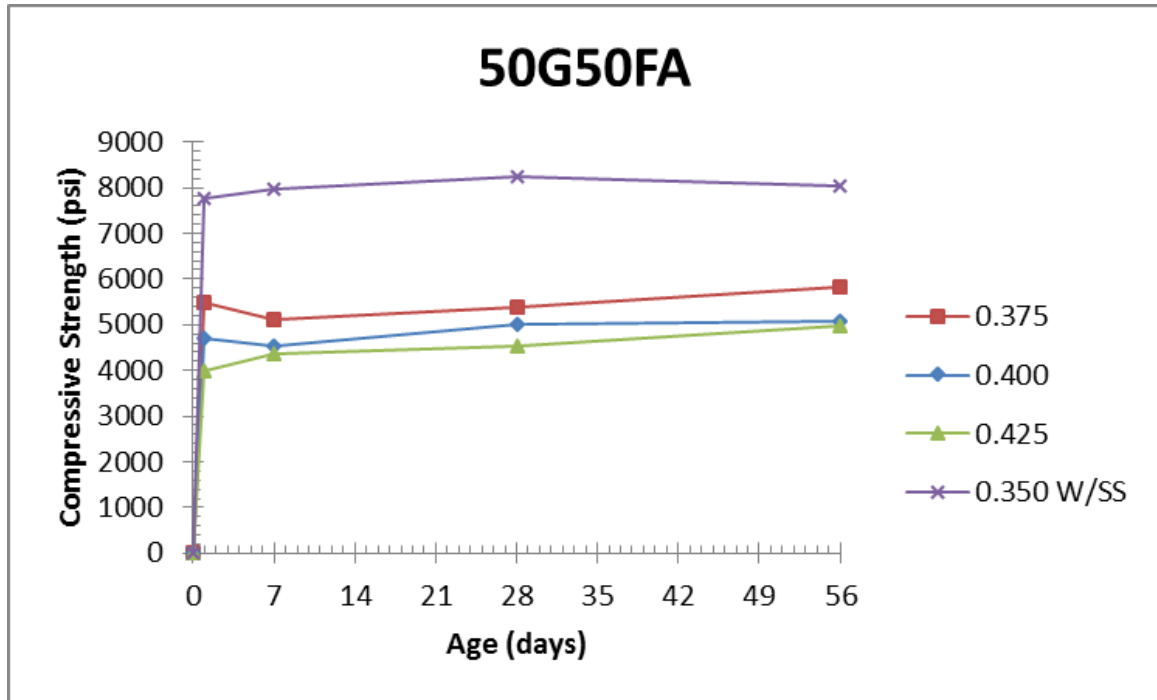


Figure 4.5: Compressive strength curve for 50G50FA mixtures.

The compressive strength of the sodium silicate mixture (around 8000 psi) was nearly double that of the sodium hydroxide mixtures. The sodium silicate mixture had a Na/Al ratio closer to 1.0 than the sodium hydroxide mixtures (see Figure 3.7). This could be the reason for higher strengths compared to the 75G25FA mixture using sodium silicate. The reason for the drastic difference in strength compared to sodium hydroxide mixtures can again be contributed to an enhanced polymerization reaction during the production process. Individual strength curves for each of the mixtures can be seen in Appendix A.

4.3.2 50G50FA: Degree of Reaction

Degree of reaction results also showed the increased impact of water content on geopolymers containing increased fly ash content. On average, about 77% of the aluminosilicate blend reacted with the activating solution. As shown in Table 4.3, when water content increased, so did the degree of reaction. Again the lowest degree of reaction occurred when the least amount of water was present. The inverse correlation with compressive strength was not an expected result, but seemed to be consistent between mixtures.

Table 4.3: Degree of reaction results for 50G50FA mixtures.

Water-Solids Ratio	Average α (%)	Standard Deviation
0.375	75.6	0.0094
0.400	77.0	0.0030
0.425	79.5	0.0070

4.3.3 50G50FA: Microstructural Analysis

There did not seem to be any major differences between the microstructure of the geopolymers as the water-solids ratio changed from 0.375 to 0.425. Microstructural images, shown in Figure 4.6, were all smooth and homogeneous with very few unreacted particles visible; this correlates to the relatively high degree of reaction results. Zeolites were present in each of the mixtures, but not in great abundance.

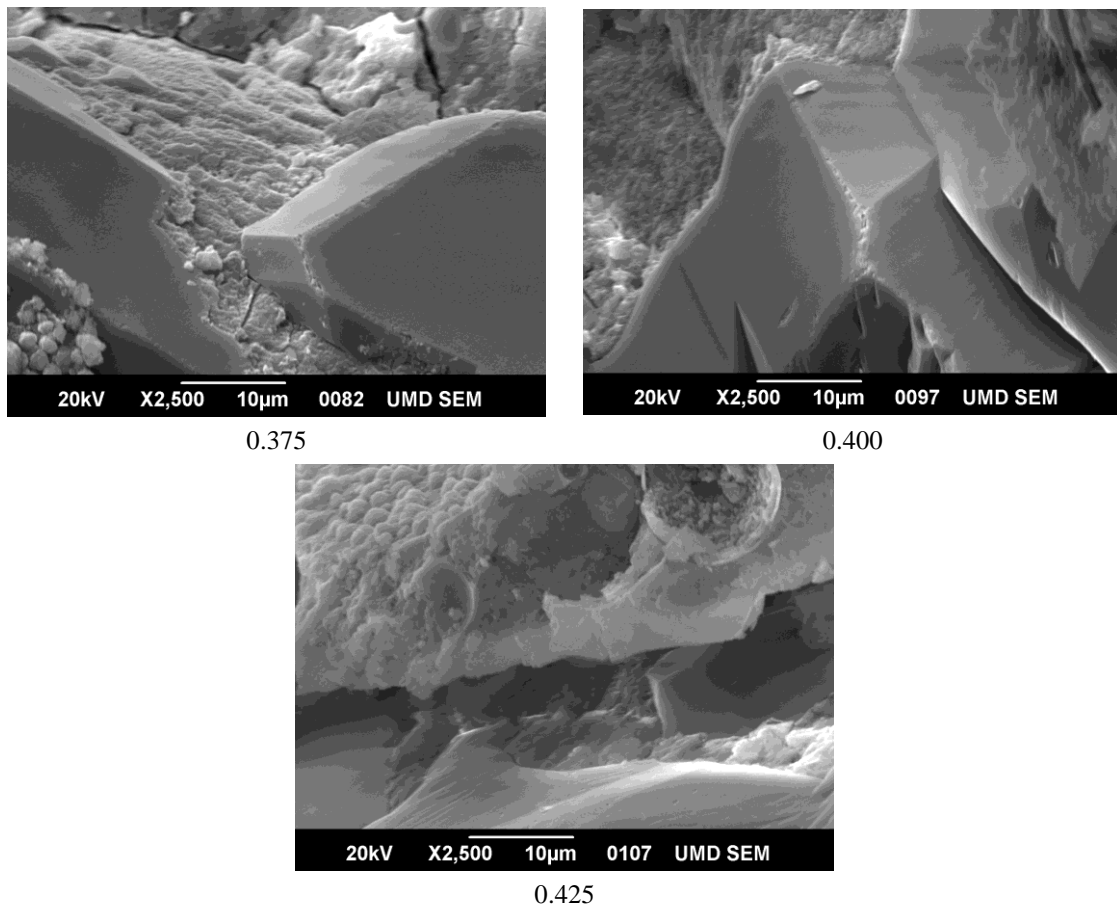


Figure 4.6: Examples of the microstructure of the 50G50FA mixtures.

4.4 25% Glass, 75% Fly Ash (25G75FA)

4.4.1 25G75FA: Compressive Strength

The 25G75FA mixture reached the lowest water-solids ratio possible without changing the mixture design ratios. The lowest water-solids ratio ($w/s = 0.350$ for NaOH activator) resulted in relatively good workability and good consolidation. Strengths, on the other hand were very low compared to the other mixtures, as shown in Figure 4.7.

Even though the strengths were low, the influence of the water-solids ratio on compressive strength could still be observed. The lower strengths could be due to mixture design constraints. In order to compare the mixtures to each other, the design ratios (aggregate: aluminosilicate and activator: aluminosilicate ratios specifically) were kept constant; this limited the 25G75FA and 100FA mixtures and prevented the w/s ratio from decreasing to the point based solely on workability. The spike in compressive strength at 1 day and decrease at 7 days for the mixture with the water-solids ratio of 0.400 is believed to be due to a malfunction of the compressive strength test machine.

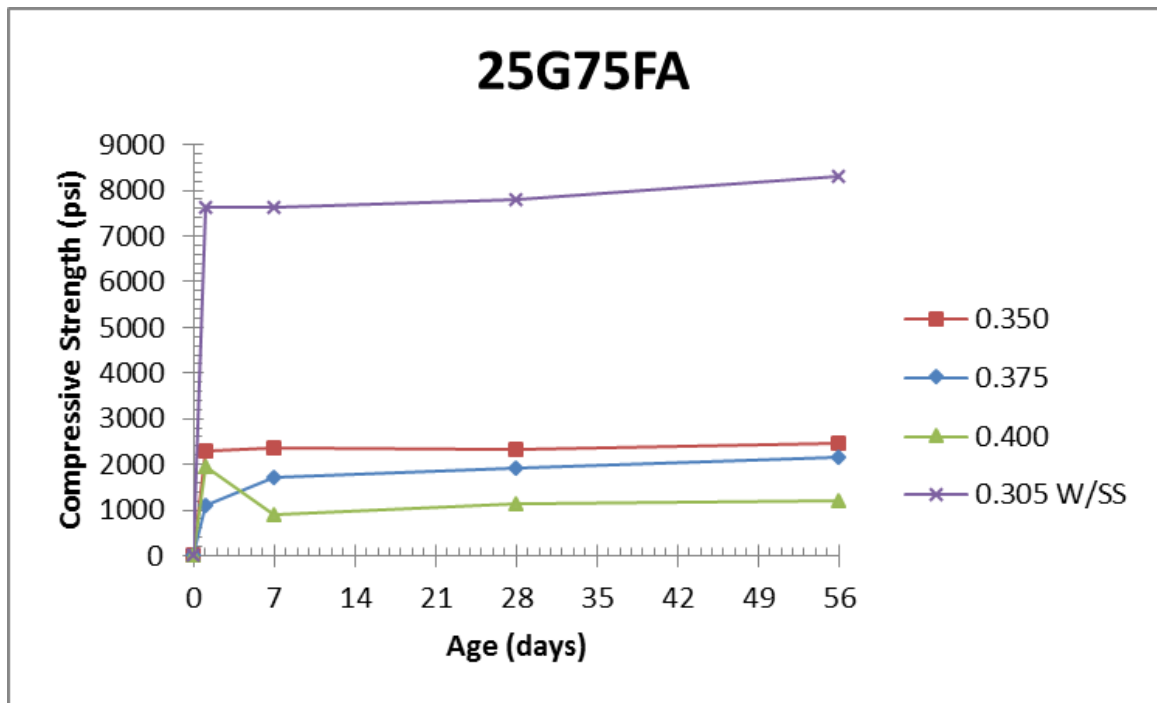


Figure 4.7: Compressive strength curve for 25G75FA mixtures.

The sodium silicate mixture achieved the highest compressive strength recorded during this research, reaching 8300 psi at 56 days. As displayed in this research, the water-solids

ratio affects the compressive strength of geopolymers. One reason this particular mixture achieved the highest strength could be due to the fact that it reached the lowest water-solids ratio possible due to mixture design constraints. The 100FA mixture (see Section 4.5) using sodium silicate in the activator did not achieve strengths as high as the 25G75FA mixture, indicating that the water-solids ratio may have been too high. Individual strength curves for the mixtures can be seen in Appendix A.

4.4.2 25G75FA: Degree of Reaction

As Table 4.4 indicates, the degree of reaction results show only a small impact from the changing water-solids ratio. The average degree of reaction was about 75%. There was not a large difference in the degree of reaction when comparing the mixtures with water-solids ratios of 0.375 and 0.400 (only 0.4%). However, the degree of reaction in the mixture with a water-solids ratio of 0.350 was nearly 2.5% lower than the other two, displaying once again the inverse correlation between compressive strength and the degree of reaction.

Table 4.4: Degree of reaction results for 25G75FA mixtures.

Water-Solids Ratio	Average α (%)	Standard Deviation
0.350	73.3	0.0040
0.375	75.7	0.0025
0.400	76.1	0.0041

4.4.3 25G75FA: Microstructural Analysis

The microstructures of the 25G75FA mixtures, shown in Figure 4.8, were again smooth and homogeneous, but unreacted fly ash particles were clearly visible within the matrix. Zeolites were also present in each of the mixtures and were different than in previous mixtures. Differences in zeolites that were observed are highlighted in Section 4.9. The peeling or coating seen in Figure 4.8 could be zeolites that had formed after the sample was broken (samples were tested for compressive strength at 7 days, but the actual age was much more than 7 days).

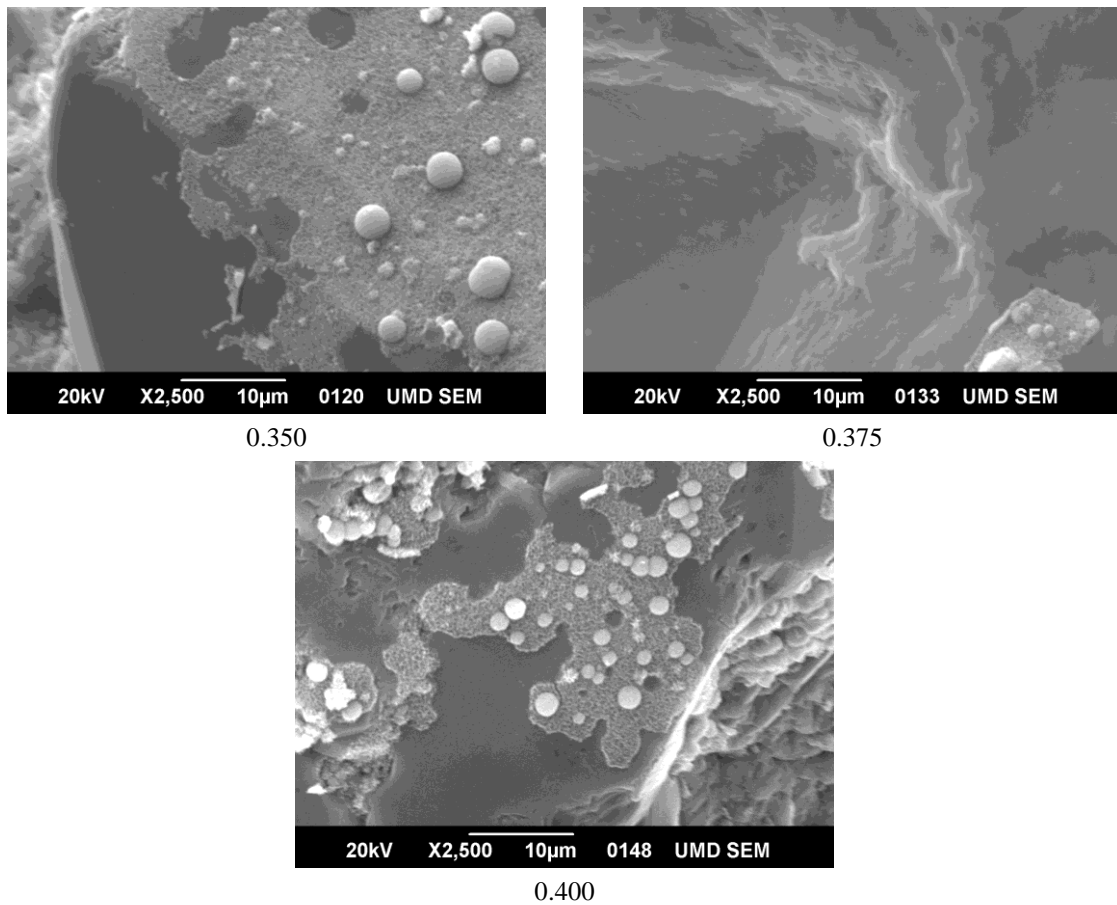


Figure 4.8: Examples of the microstructure of the 25G75FA mixtures.

4.5 100% Fly Ash (100FA)

4.5.1 100FA: Compressive Strength

The 100% Class F fly ash mixture also included the lowest water-solids ratio possible without changing the mixture design ratios. Strengths were very low, but like the 75G25FA mixture, the water-solids ratio seemed to have only a slight impact on compressive strength (see Figure 4.9). The 100FA mixture reached the minimum water-solids ratio, so the fact that mixture design ratios could not be altered is thought to have played a role in the lower compressive strengths. An increase in strength did not occur

over the 56-day period for any of the mixtures. However, extra samples were cast at each water-solids ratio and significant strength gains (approximately 400 psi in each mixture) were observed up to 198 days (see Appendix A).

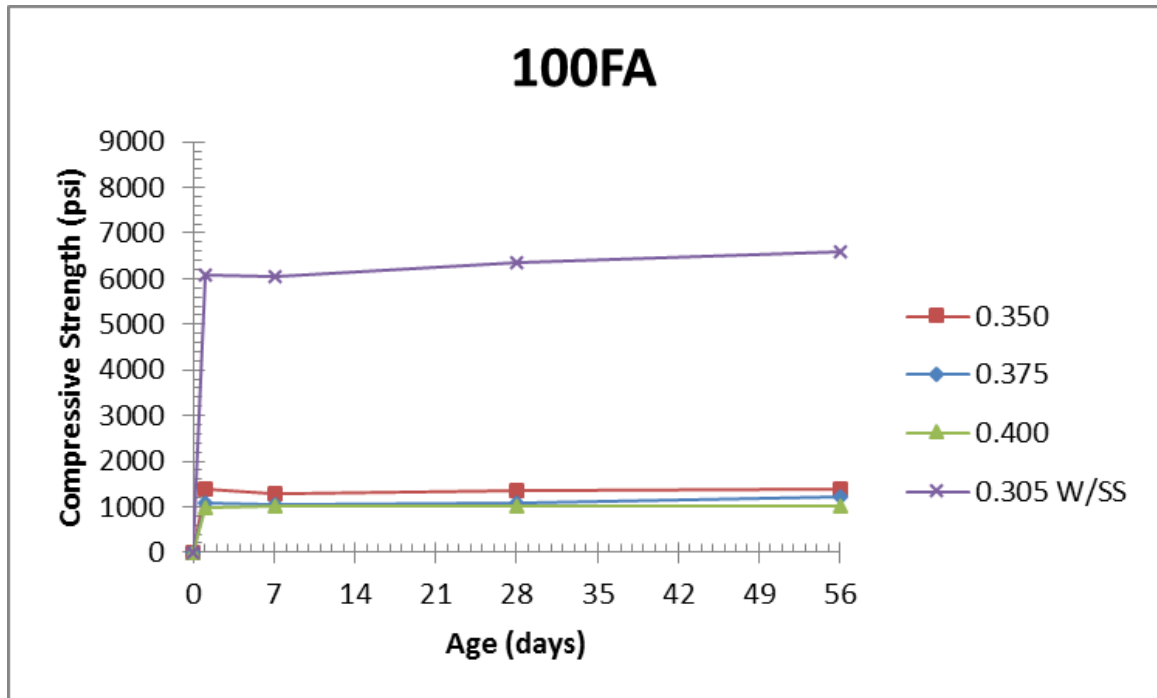


Figure 4.9: Compressive strength curves for 100FA mixtures.

When using 100% Class F fly ash, the compressive strength for the sodium silicate mixture was about six times higher than the sodium hydroxide mixtures and slightly higher than the 100% glass mixtures (see Section 4.1). The sodium silicate mixture using 100% fly ash also set in a matter of minutes. A quick setting time is consistent with other research (Sofi et al. 2007) and can cause problems in practical applications. Individual strength curves for the mixtures can be seen in Appendix A.

4.5.2 100FA: Degree of Reaction

As Table 4.5 shows, there was a small influence on the degree of reaction when changing the water-solids ratio. On average, about 74% of the fly ash reacted. The 0.400 water-solids ratio mixture had a relatively higher degree of reaction than the other two mixtures, but the 0.350 and 0.375 water-solids ratios had degrees of reaction that were almost identical. Again, this could be contributed to keeping mixture design ratios consistent throughout the research.

Table 4.5: Degree of reaction results for 100FA mixtures.

Water-Solids Ratio	Average α (%)	Standard Deviation
0.350	72.6	0.0081
0.375	72.9	0.0033
0.400	76.1	0.0063

4.5.3 100FA: Microstructural Analysis

Images of the 100FA microstructures, shown in Figure 4.10, appear slightly different between the mixtures as the water-solids ratio changed from 0.350 to 0.400. All microstructures seemed to be heterogeneous compared to other mixture types. Again, a peeling or coating of zeolites is observed as in the 25G75FA mixture. Zeolites were very abundant and different compared to previous mixtures (see Section 4.9).

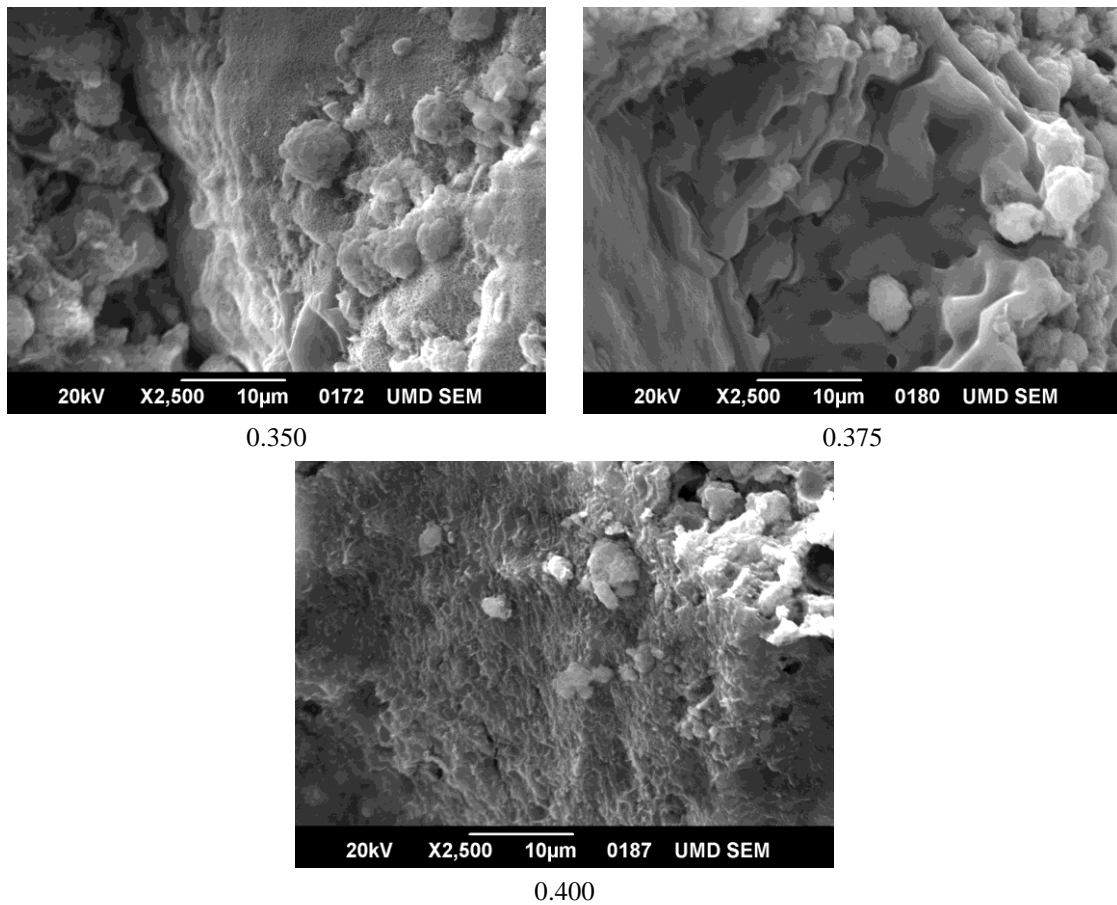


Figure 4.10: Examples of the microstructure of the 100FA mixtures.

4.6 Mixture Composition Comparison

The following sections include observations made between the various mixtures (100G, 75G25FA, etc.).

4.6.1 Compressive Strength

As shown by compressive strength curves in the previous sections (Sections 4.1-4.5), a majority of the compressive strength for the geopolymer mortars tested was gained within the first 24 hours. This is primarily due to the heat cure provided after mixing and the fact that most of the reactions occur during that time. There was not a large amount of

strength gain within the first 56 days after the heat cure, unlike what has been observed in other studies (Duxson et al. 2007; Sofi et al. 2007). However, extra samples of 75FA25G and 100FA mixtures were cast after not seeing a lot of strength gain from other mixtures. Most of the extra samples exhibited a large amount of strength gain (See Appendix A).

The 7-day compressive strength of each of the mixture compositions activated with NaOH for each of the water-solids ratios are compared in Figure 4.11. Seven days was selected because compressive strengths generally plateau after seven days and degree of reaction tests were conducted on 7-day old test samples. This figure reflects previous conclusions that when adding fly ash to waste glass based geopolymers, the water-solids ratio appears to influence compressive strength to a greater extent.

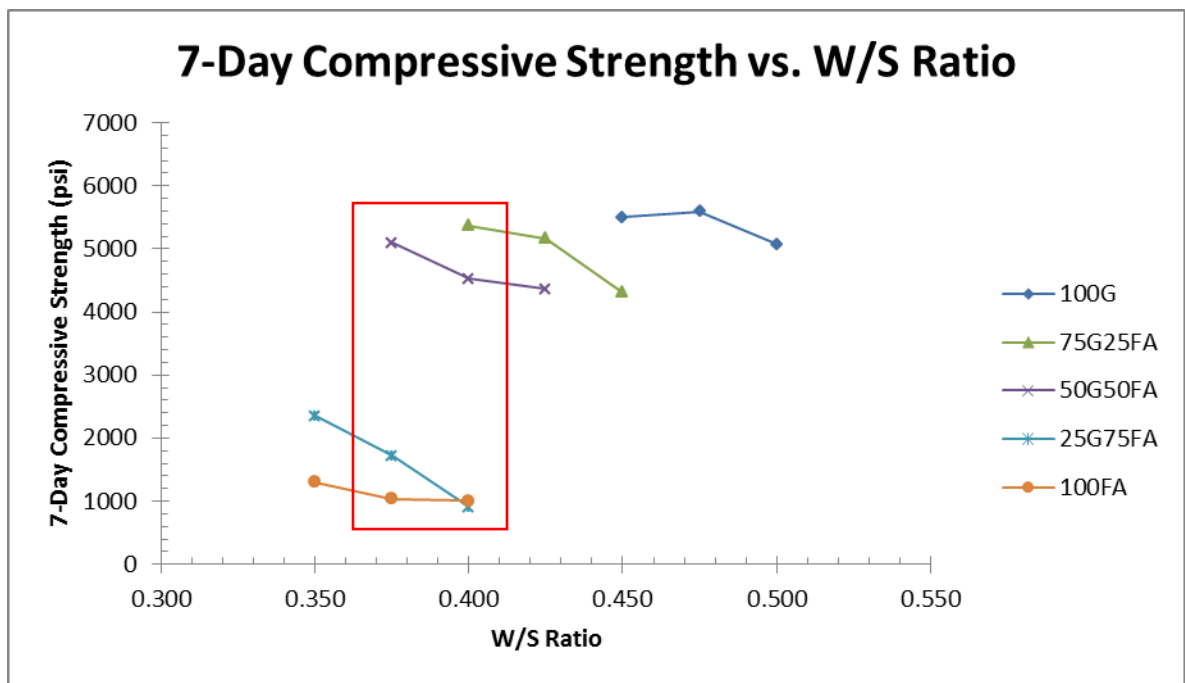


Figure 4.11: Compressive strength trends as water-solids ratio changes in mixtures at 7 days.

Figure 4.11 also illustrates how dependent the overall effect of the water-solids ratio is on mixture composition. For the most part, as the water-solids ratio increases, compressive strength decreases. This trend is more obvious in some mixtures than it is in others (see 75G25FA vs. 100FA), but in general this conclusion holds true.

It was also observed that as the fly ash content increases, and all other variables remain constant, compressive strength decreases. This is shown very clearly when examining water-solids ratios 0.350 and 0.425, where a direct comparison between the mixtures can be made (see boxed data points in Figure 4.11). At a 0.400 water-solids ratio, the mixtures containing 25% and 50% fly ash perform well. However, the mixtures containing 75% and 100% fly ash struggle to reach strengths higher than 1000 psi. The mixtures containing large amounts of fly ash, which exhibited low strengths, were likely low because there was too much water in the mixture due to mixture design constraints that were kept constant throughout this research (see Section 3.2.5). Compressive strength vs. water-solids ratio curves recorded at 1, 28, and 56 days can be seen in Appendix A.

4.6.2 Degree of Reaction

The expected correlation between compressive strength and degree of reaction was that mixtures with a higher degree of reaction would yield higher compressive strengths. This was hypothesized based on the idea that the more particles that dissolve and react, the more geopolymer phase material is formed, which will yield a stronger binder. This was

not evident with any of the individual mixtures, nor when comparing mixture composition. As Figure 4.12 shows, the opposite actually occurred. Higher compressive strengths resulted from mixtures with lower degrees of reaction. The expected correlation between mixture compositions (relating to degree of reaction and compressive strength) would have been indicated by relatively straight, positively sloped lines.

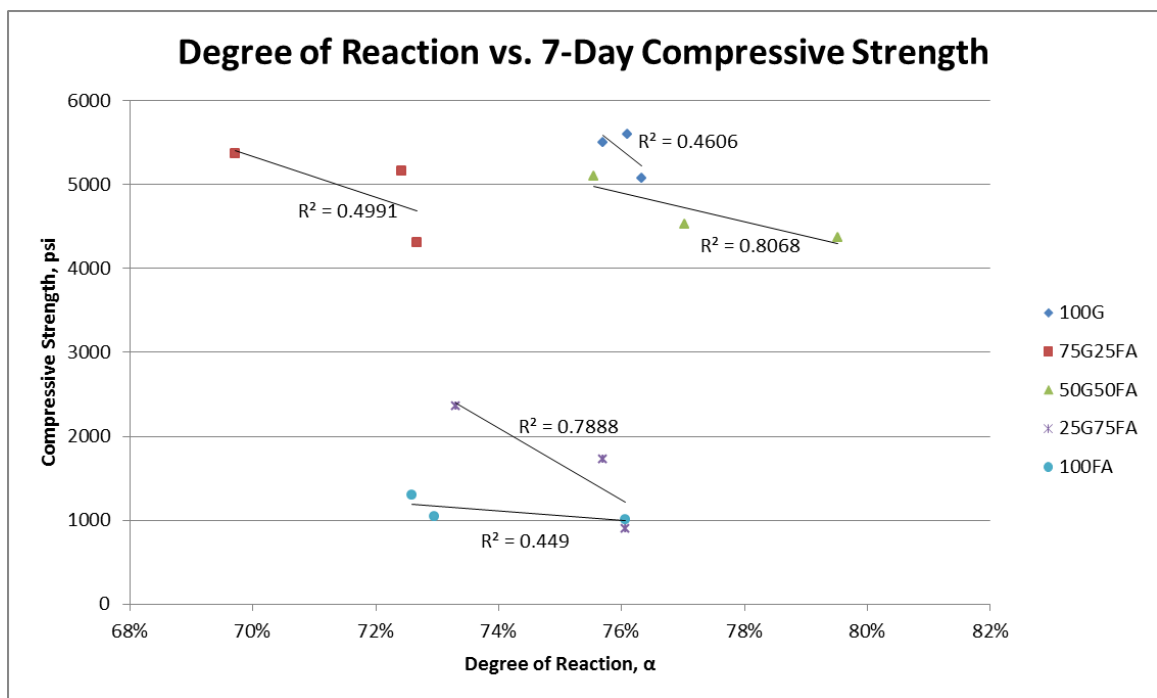


Figure 4.12: Degree of reaction vs 7-day compressive strength.

When looking at degree of reaction, the results showed that the degree of reaction may be more dependent on mixture composition. This is shown in Table 4.6 where, outside of the 75G25FA mixture, the degree of reaction results appear to correlate with the composition trend (i.e. as fly ash increases degree of reaction decreases). This conclusion can likely be attributed to the fact that water is simply a medium for the reaction mechanisms to occur

rather than a hydration requirement like it is for portland cement. There is also a margin of error that is caused by crystalline material in the fly ash that may not dissolve in the hydrochloric acid. This means that while 100% of the glass in the mixture has the potential to react, not all of the fly ash can. Therefore, degree of reaction results may not be direct representations of the dissolution reactions. In other words, the available reactive phases in glass and fly ash are different and can affect degree of reaction results.

Table 4.6: Comparison between degree of reaction (DOR) and 7-day compressive strength.

Mixture Composition	DOR Range (%)	Max. 7-Day Compressive Strength (psi)
100G	75.7-76.3	5597
75G25FA	69.7-72.7	5372
50G50FA	75.6-79.5	5098
25G75FA	73.3-76.1	2355
100FA	72.6-76.1	1302

4.6.3 Microstructural Analysis

A comparison of the microstructure of all of the compositions and water-solids ratios used in the NaOH mixtures is shown in Figure . As the water-solids ratio changed within each mixture type, the difference in microstructure was negligible. However, the microstructures did change as the composition (fly ash to glass ratio) changed, this is similar to results from compressive strength and degree of reaction tests. This observation is especially noticeable when comparing the 100G and 75G25FA mixtures. The 100% glass mixture had fewer observable unreacted particles than the other two mixtures and did not contain an abundance of zeolites. The 75G25FA mixture had noticeable amounts

of zeolites and unreacted particles, but managed to have a relatively smooth and homogenous microstructure.

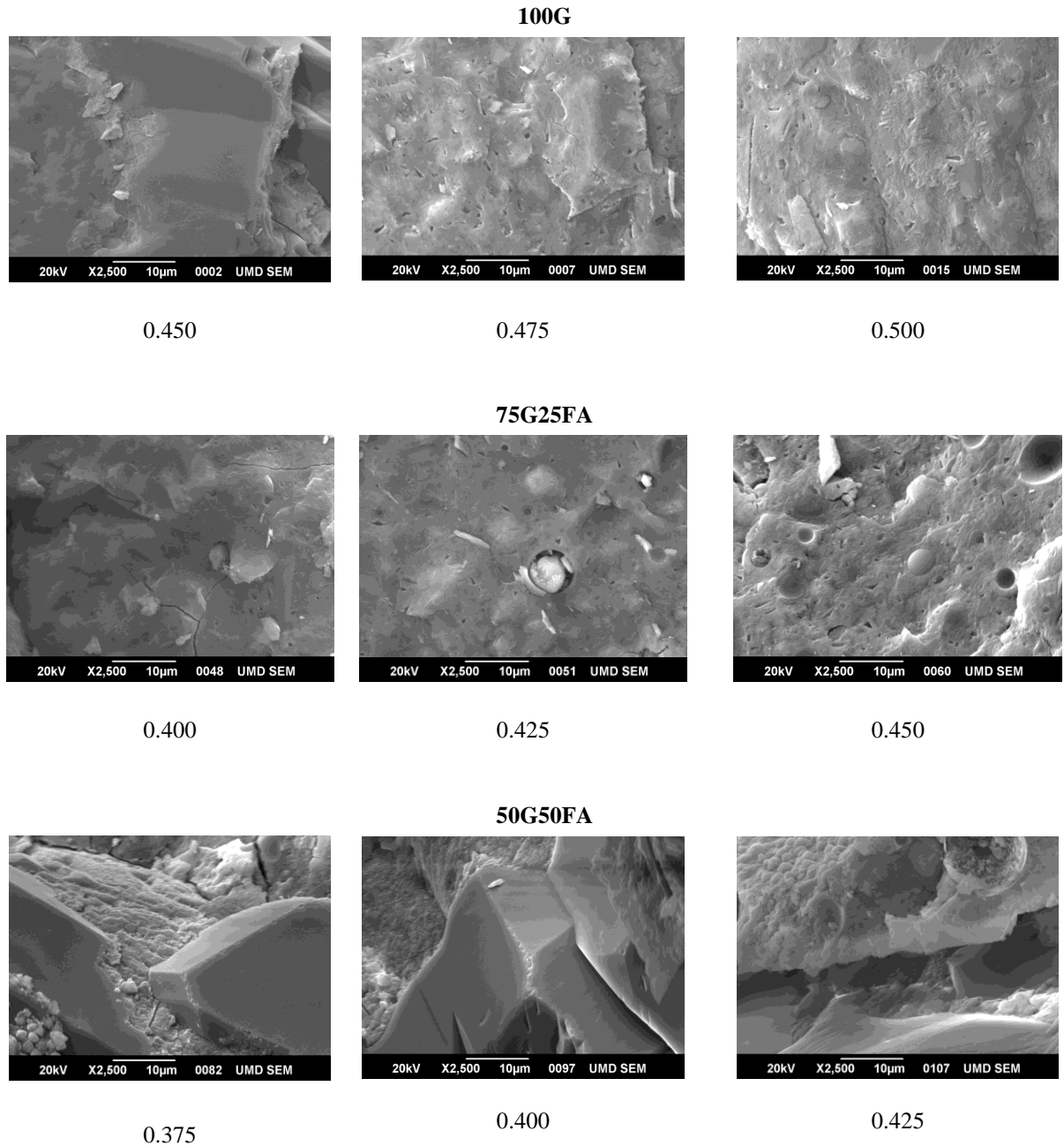


Figure 4.13: Microstructural comparisons between mixture compositions.

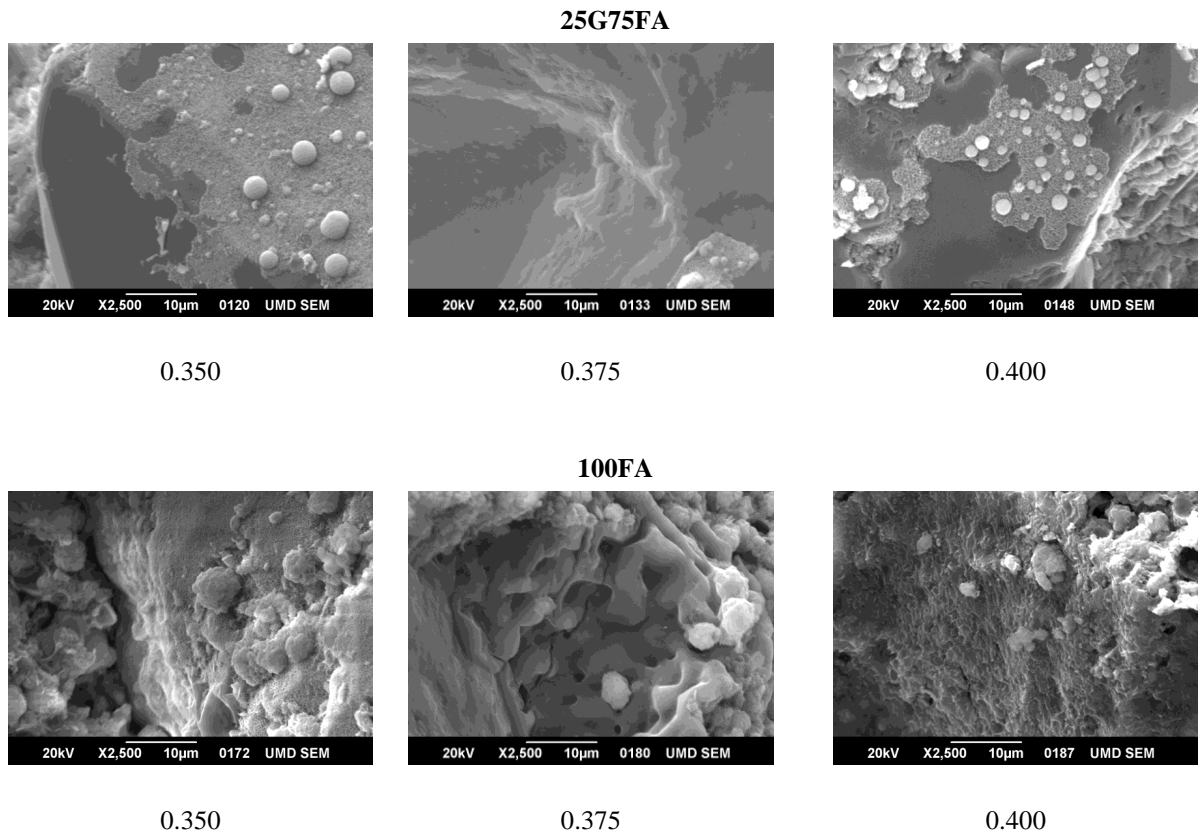


Figure 4.13 (continued): Microstructural comparisons between mixture compositions.

During the microstructural examination, an increase in zeolites present on the surface of the samples was observed in the 100FA mixtures compared to 25G75FA mixtures. In the 25G75FA mixture, some of the geopolymer product was visible underneath zeolites forming on the surface in each of the images. However, the 100FA mixture seemed to have zeolites forming over the entire geopolymer product. Zeolites can form in geopolymer mixtures with excess water, but both mixture compositions used the same water-solids ratios. However, the fact that those water-solids ratios were the lowest

achievable due to mixture design constraints, and not workability, implies that there might have been too much water in the 100FA mixture, which theoretically could have used lower water-solids ratios, in a way confirming the microstructural analysis.

4.7 Sodium Silicate Mixtures

The degree of reaction results from the sodium silicate mixtures yielded similar conclusions as those for the sodium hydroxide mixtures, but on a more extreme scale.

Only one water-solids ratio was tested for each sodium silicate mixture, so definitive trends involving the effects of the water-solids ratio on a sodium silicate activator could not be made. However, the degree of reaction was generally much lower for sodium silicate mixtures compared to sodium hydroxide mixtures, and compressive strengths for sodium silicate mixtures were generally much higher than those of sodium hydroxide mixtures as was found in a similar study (Criado et al. 2007). The degree of reaction and compressive strength test results for sodium silicate mixtures is shown in Table 4.7.

Trends regarding the composition of the mixtures could not definitively be made without changing mixture design constraints to allow for lower water-solids ratios in the 25G75FA and 100FA mixtures. However, when only considering 100G, 75G25FA, and 50G50FA mixtures, results showed that as fly ash content increased, compressive strength and degree of reaction also increased (shown in Figure 4.14).

Table 4.7: Comparison between degree of reaction (DOR) and 7-day compressive strength of sodium silicate mixtures.

Mixture Composition	DOR (%)	7-Day Compressive Strength (psi)
100G	41.7	5197
75G25FA	58.3	6525
50G50FA	67.1	7981
25G75FA	66.1	7614
100FA	66.7	6040

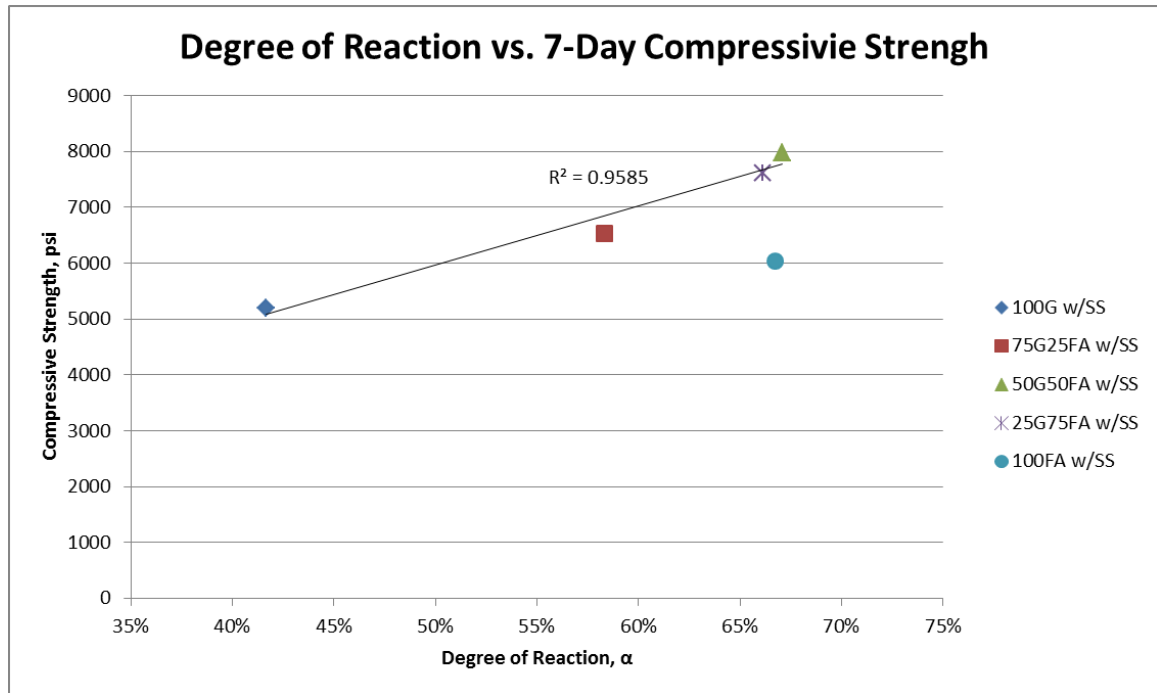


Figure 4.14: Degree of reaction vs. 7-day compressive strength of sodium silicate mixtures.

The degree of reaction in the sodium silicate mixtures was much lower than in the mixtures activated with sodium hydroxide because of the presence of pre-dissolved silica. Since there is already a fairly significant amount of silica in solution, less dissolution is

required to reach a supersaturated solution (Criado et al. 2007). This means that less dissolution occurs and less of the aluminosilicate source reacts (see Section 2.4.3). This was found to be true in all five mixtures, as shown in Figure 4.15.

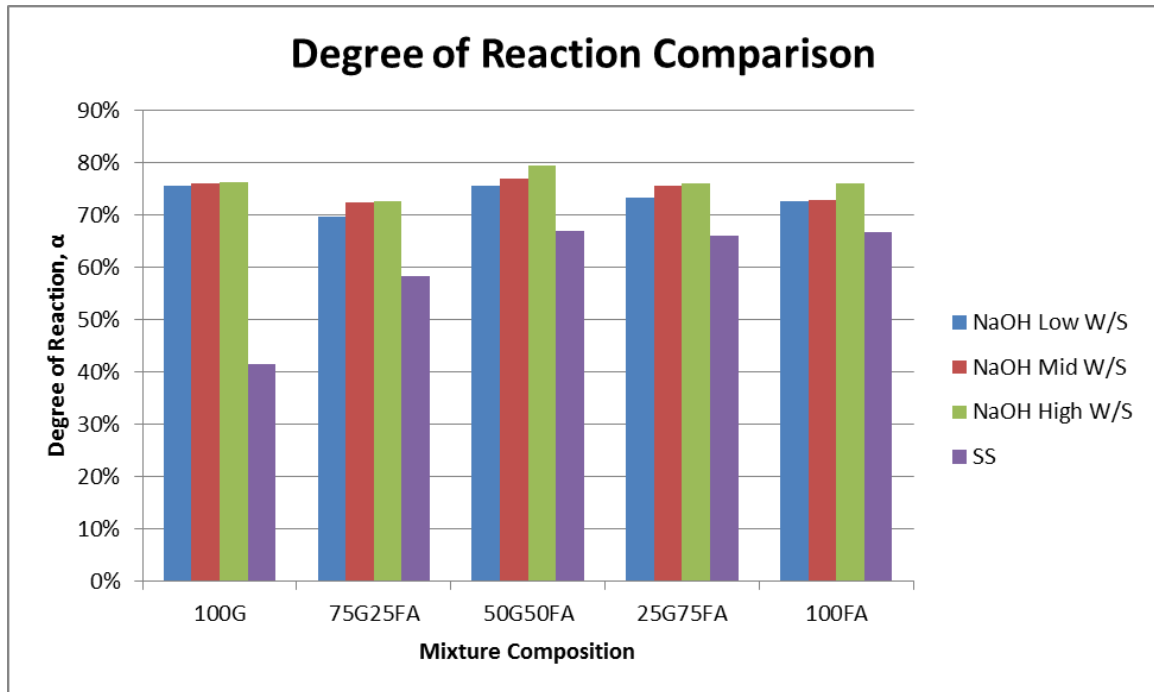


Figure 4.15: Sodium hydroxide DOR results compared to sodium silicate DOR results.

During the microstructural analysis of the mixtures including sodium silicate, many interesting formations were observed that were not observed in the mixtures activated solely with sodium hydroxide. These formations could not definitively be classified as zeolites. Examples of these formations are shown in Figure 4.16.

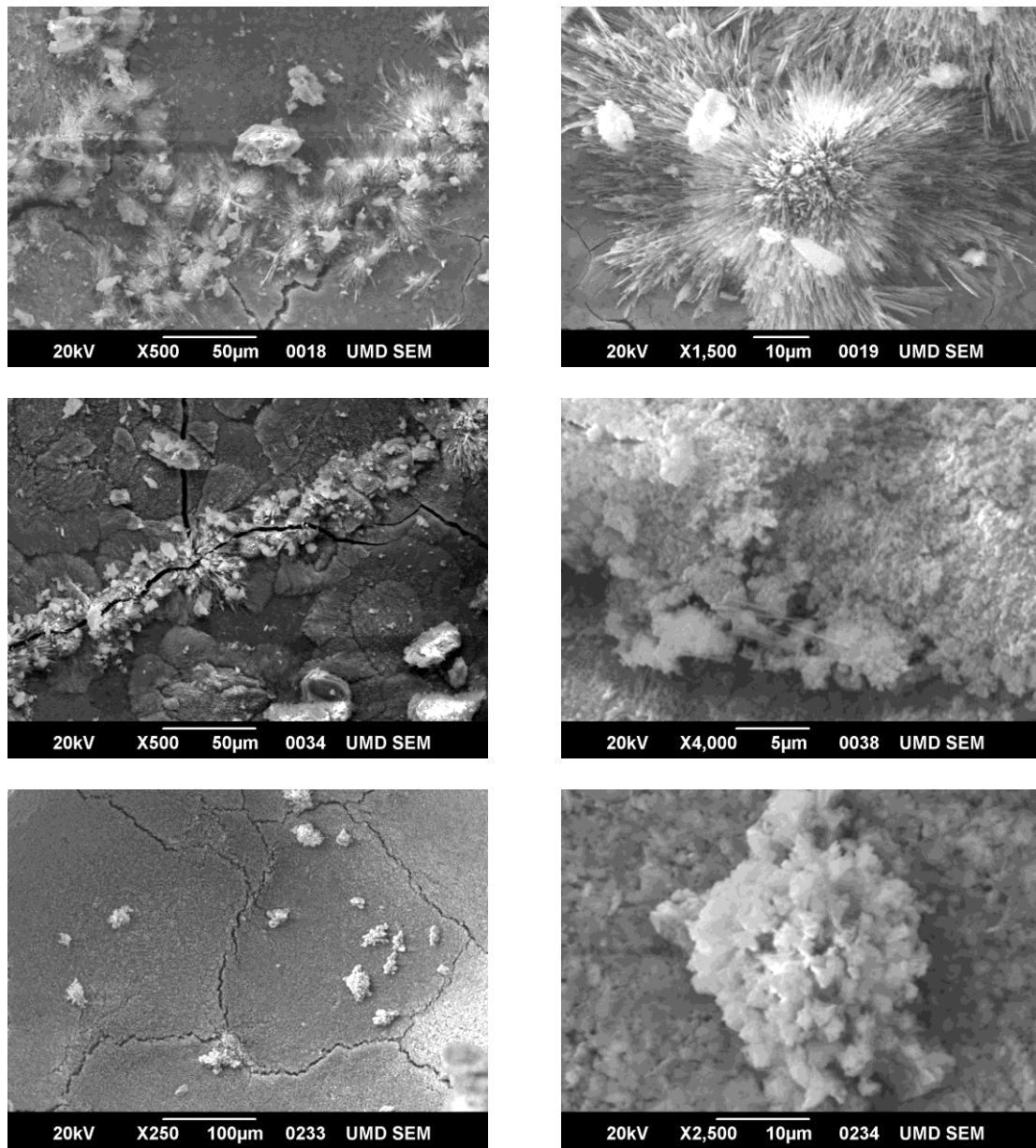
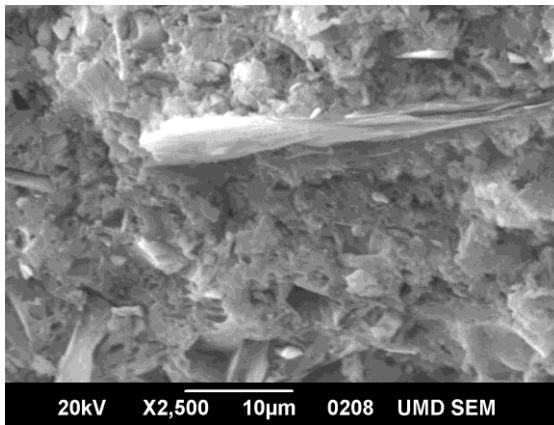


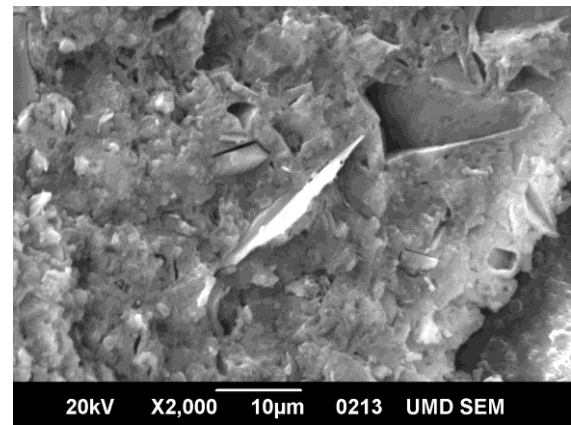
Figure 4.16: Phases observed during microstructural analysis of sodium silicate mixtures that were not observed during analysis of NaOH-activated mixtures.

4.8 Unreacted Particles

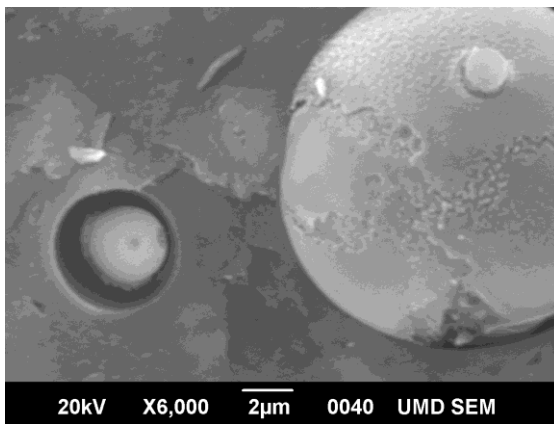
A relatively smooth microstructure was consistent across all NaOH mixtures. However, in mixture containing fly ash, as the fly ash content increased, so did the quantity of unreacted particles visible at the surface. Unreacted particles were also of interest when examining the microstructures in an attempt to confirm degree of reaction test results. Unreacted or partially reacted glass, fly ash, and metakaolin particles (see Figure 4.17) were observed in most of the mixtures. Also, in mixtures using sodium silicate as an activator, where degree of reaction was lower, even more unreacted particles were present as was found in a similar study (Criado et al. 2007). Their abundance confirms that the degree of reaction results were qualitatively accurate.



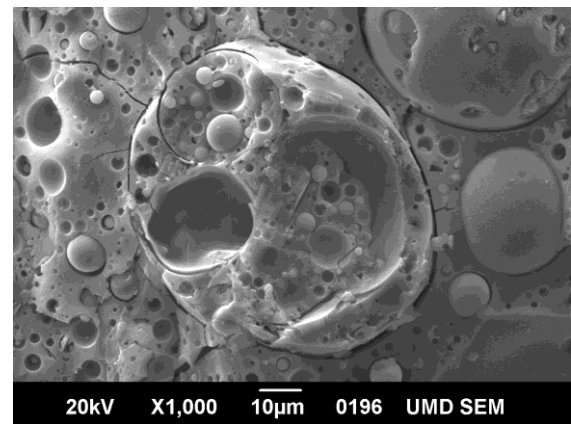
A



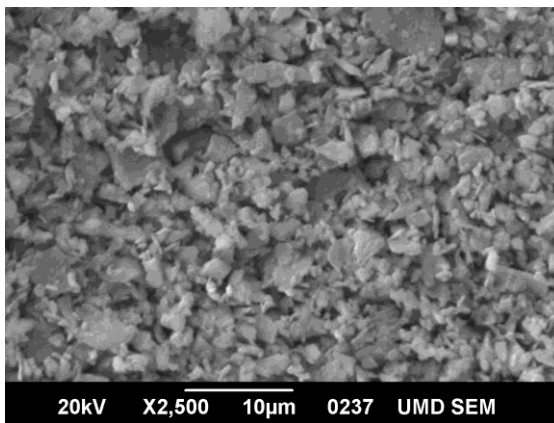
B



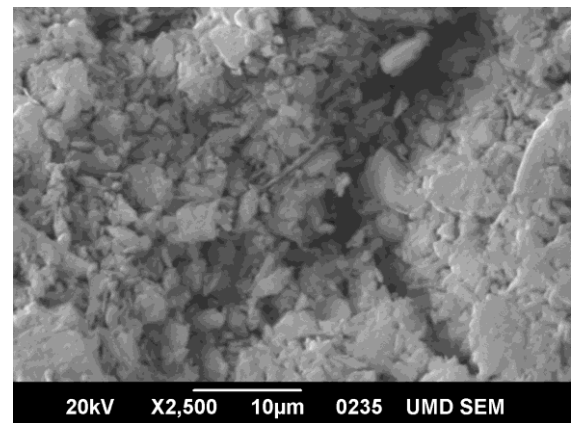
C



D



E



F

Figure 4.17: Unreacted glass (A, B), fly ash (C, D), and metakaolin (E, F) particles observed during microstructural analysis.

4.9 Zeolites

Another area of interest was the formation of zeolites in mixtures where the water-solids ratio may have been higher than optimal. Different types of zeolites (see Figure 4.18) were observed depending on the mixture composition and w/s ratio. There also seemed to be more zeolites in the mixtures using sodium hydroxide as the activating solution compared to the sodium silicate mixtures (Criado et al. 2007). This is due to the faster polymerization reactions from the presence of pre-dissolved silica (see Section 2.4.3).

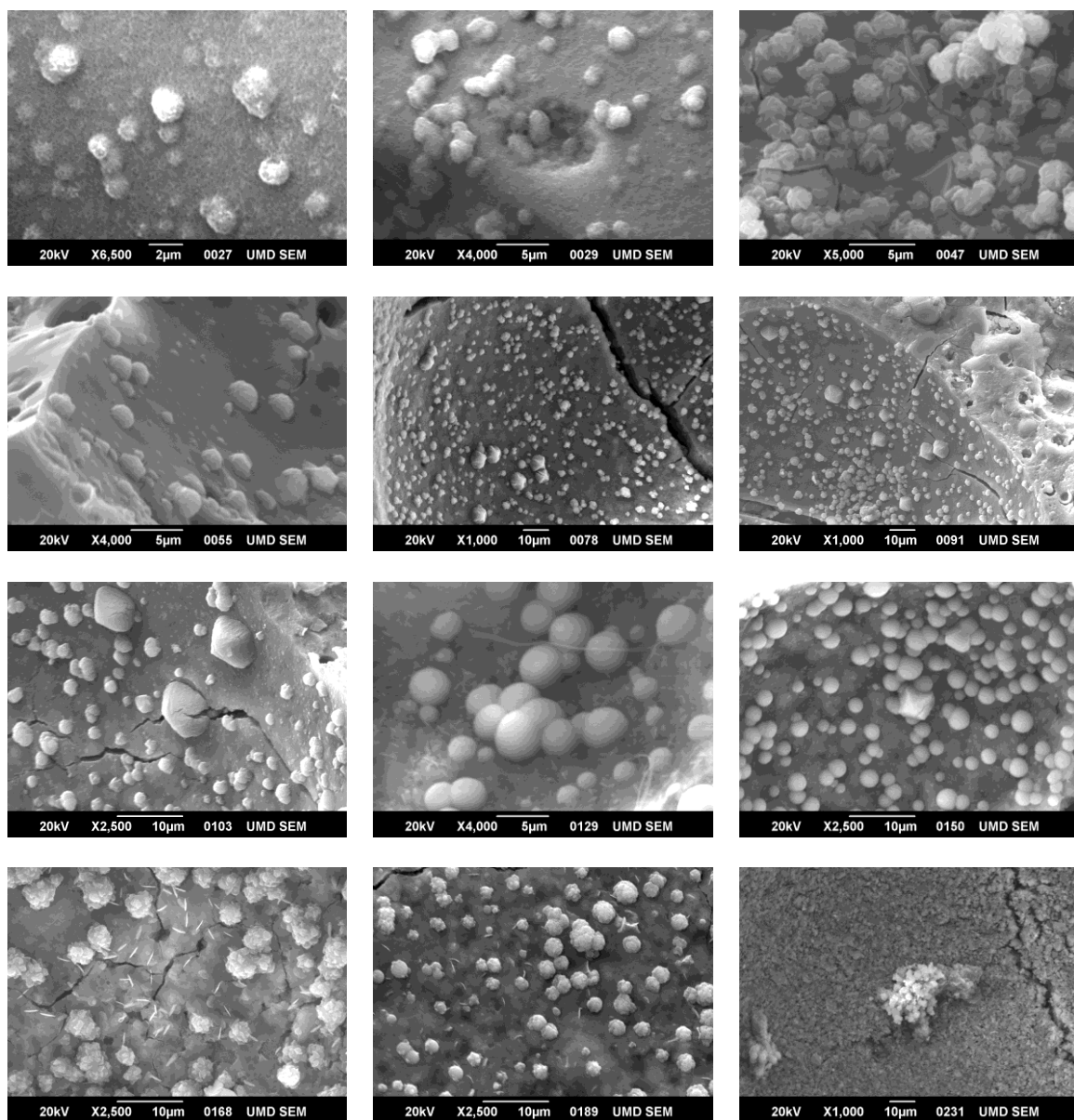


Figure 4.18: Variety of zeolites observed during microstructural analysis.

5 Conclusions and Discussion

The role that water plays in portland cement concrete is well known and understood. The ratio of water to cementitious materials directly affects the performance of portland cement concrete in areas such as strength and durability. Water acts as a reaction medium for the major cement phases to react with each other during hydration and is essential for the concrete to cure properly. It is also chemically bound within the hydration products. This is the major difference between the role of water in portland cement concrete and geopolymers. In a geopolymer, water is not chemically bound to the reaction products, it is consumed during dissolution and then expelled back into the mixture through a condensation reaction. This cycle continues until the silica and alumina ions are bonded together in the N-A-S-H gel. The leftover water exists beside the reaction products instead of within the reaction products. This research aimed to determine the effect of the water-solids ratio on the compressive strength and degree of reaction of fly ash-waste glass geopolymers and if the effect was similar to how water affects portland cement.

Five geopolymer mixtures composed of varying amounts of waste glass and fly ash were examined and three water-solids ratios were used for each mixture. Samples were tested for compressive strength and degree of reaction, and examined under a scanning electron microscope. Sodium hydroxide was used as the activating solution for most of the mixtures, and a combination of sodium hydroxide and sodium silicate was used for one mixture at each composition.

5.1 Compressive Strength

The compressive strength results showed that in most mixtures, changing the water content had an effect on compressive strength. Mixtures using a combination of aluminosilicate sources (ex. 75G25FA) showed higher compressive strengths at lower water-solids ratios, which were the expected results. However, the 100G and 100FA mixtures were not significantly affected by the changing water-solids ratio. The noticeable sensitivity between mixtures could be due to a variety of differences between the materials. Particle size and shape are very different between the materials used in this research and as Section 4 shows, when these materials are blended together, the water-solids ratio has an increased effect on compressive strength. Atomic structure and composition can also be a factor for the increased sensitivity noted in Section 4. Glass particles are more uniform from particle to particle in composition and on a molecular level compared to fly ash. Fly ash also contains crystalline phases, meaning the entire particle may not break down during dissolution. When dissolution takes place, depending on how well and how much of the particle dissolves, the Si/Al and Na/Al ratios can be very different in the gel surrounding each particle. If the gel is not uniform due to different molar ratios, local failures could occur near particles surrounded by weaker geopolymer product. The fly ash used in this research can also react with leftover calcium in the mixtures consisting of glass-fly ash blends, creating a C-A-S-H gel instead of the N-A-S-H gel discussed in Section 2.4.

5.2 Degree of Reaction

The expected result of the degree of reaction investigation was that a higher degree of reaction would correlate with higher compressive strengths. However, the opposite result was consistent in essentially all NaOH mixtures. Degree of reaction results showed the percentage of reacted particles decreased as the water-solids ratio decreased in mixtures containing a blend of waste glass and fly ash. This could be due to the fact that water acts as a reaction medium and not chemically bound to the reaction products. If the concentration of the activator is high enough, a higher water-solids ratio will accelerate the dissolution phase and more particles will react (Zuhua et al. 2009). However, a better understanding of the degree of reaction test procedure and how accurately the results represent dissolution of fly ash particles is required. As discussed in Section 4.6.2, crystalline phases in fly ash can cause discrepancies in degree of reaction results.

5.3 Microstructural Analysis

Microstructure images showed a relatively homogeneous geopolymer product in each mixture. Zeolites were observed in a majority of air voids and unreacted particles were present and correlated with degree of reaction results. “Pull-out” locations were also observed in samples with higher water-solids ratios (see 75G25FA in Figure Figure 4.13). These locations appeared to be from unreacted particles that were present before the sample was broken. This observation could mean that the addition of more water decreases the strength of the geopolymer at the interfacial transition zone of unreacted

particles. The interfacial transition zone was not examined in this research, so more research is required to determine what the ITZ consists of in geopolymers.

5.4 Mixture Composition

A comparison of how changing the water-solids ratio affects strength and degree of reaction between mixture compositions showed that as fly ash content increased, compressive strength decreased, assuming all other variables were held constant. However, the amount of water required also decreased as fly ash content increased and this was not allowed past a certain point due to pre-determined design constraints. The degree of reaction results did not indicate the expected correlation between compressive strength and mixture composition where a higher degree of reaction would result in a higher compressive strength.

Sodium silicate mixtures were also examined for each mixture composition. The addition of sodium silicate allowed for a lower water-solids ratio at a similar consistency for all of the mixtures tested in this research. Compressive strengths were generally higher and the degree of reaction was significantly lower due to pre-dissolved silica in the activator.

5.5 Summary and Future Research

Geopolymers have the potential to be a viable alternative or supplemental binder to portland cement. The chemical composition of the aluminosilicate source and the composition and concentration of the activating solution are key parameters that affect how well the geopolymer performs. The water content also affects performance, as

investigated in this research. Higher compressive strengths were observed in mixtures with lower water-solids ratios. Mixtures with lower water-solids ratios also exhibited lower degrees of reaction.

There are still a lot of unknowns about geopolymers, meaning continued research is essential for geopolymer technology to become a viable infrastructure material. Some topics of future research that are related to this project include:

- Investigate the accuracy of the degree of reaction test. Conduct a “confidence test” consisting of preliminary degree of reaction tests on initial aluminosilicate materials (glass, fly ash, etc.) to determine the amount of aluminosilicate actually available for dissolution.
- Continue research on how the water-solids ratio affects mixtures activated by sodium silicate. This research only examined one water-solids ratio for each composition.
- Apply the same research program to a series of mixtures with a wider range of w/s ratios than were tested here to determine an optimum curve for water-solids ratios and expand material selection to see how other aluminosilicate materials are affected.
- Investigate the effect of water-solids ratio using different mixture design ratios. Changing individual mixture design parameters such as activator/aluminosilicate ratio or sodium silicate/NaOH ratio can provide information as to how each component affects performance.

- Discover the optimal curing time and temperature for geopolymers. There have been studies conducted that compare curing conditions (Zuhua et al. 2009) for a single mixture, but there may be different curing conditions required for different materials.
- Investigate the effect of admixtures on various geopolymer mixtures. If, for example, water reducers, do work on geopolymer concretes, how low of a w/s ratio can be used to still make quality concrete?

6 References

1. ASCE, American Society of Civil Engineers. 2013. 2013 report card for america's infrastructure. 2013.
2. ASTM C1157 AI. 2008. ASTM C1157-08 standard performance specification for hydraulic cement. .
3. ASTM C150 AI. 2005. ASTM C150-05 standard specification for portland cement. .
4. ASTM C192 AI. 2012. ASTM C192/C192M-12 standard practice for making and curing concrete test specimens in the laboratory. .
5. ASTM C39 AI. 2012. ASTM C39/C39M-12 standard test method for compressive strength of cylindrical concrete specimens. .
6. ASTM C778 AI. 2013. ASTM C778-13 standard specification for standard sand. .
7. Budh CD and Warhade NR. 2014. Effect of molarity on compressive strength of geopolymer mortar. International Journal of Civil Engineering Research 5(1):83-86.
8. Christiansen MU. 2013. An investigation of waste glass-based geopolymers supplemented with alumina. Michigan Technological University.
9. Criado M, Fernandez-Jimenez A, de la Torre, A. G., Aranda MAG, Palomo A. 2007. An XRD study of the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the alkali activation of fly ash. 37:671-9.
10. Cyr M, Idir R, Poinot T. 2012. Properties of inorganic polymer (geopolymer) mortars made of glass cullet. J Mater Sci 47(6):2782-97.
11. Davidovits J. 2008. Geopolymer chemistry and applications. Saint-Quentin: Institut Geopolymere.
12. Duxson P, Fernandez-Jimenez A, Provis JL, Lukey GC, Palomo A, van Deventer, J. S. J. May 2007. Geopolymer technology: The current state of the art. Journal of Materials Science 42(9):2917,2917-2933.
13. Duxson P, Provis JL, Lukey GC, van Deventer JSJ. 2007. The role of inorganic polymer technology in the development of 'green concrete'. Cem Concr Res 37(12):1590-7.

14. Fernandez-Jimenez A and Palomo A. 2005. Composition and microstructure of alkali activated fly ash binder: Effect of the activator. 35:1984-92.
15. Fernández-Jiménez A, Palomo A, Criado M. 2005. Microstructure development of alkali-activated fly ash cement: A descriptive model. *Cem Concr Res* 35(6):1204-9.
16. Graham D and Midgley N. 2000. Triangular diagram plotting spreadsheet (TRI-PLOT). .
17. Huntzinger DN and Eatmon TD. 2009. A life-cycle assessment of portland cement manufacturing: Comparing the traditional process with alternative technologies. *J Clean Prod* 17(7).
18. Jang JG, Lee NK, Lee HK. 2014. Fresh and hardened properties of alkali-activated fly ash/slag pastes with superplasticizers. *Construction and Building Materials* :169.
19. Kosmatka SH and Wilson ML. 2011. Design and control of concrete mixtures. Fifteenth ed. Illinois: Portland Cement Association.
20. Kumar Mehta P and Monteiro PJM. 2006. Concrete microstructure, properties, and materials. 3rd ed. New York: McRaw-Hill.
21. Mamlouk MS and Zaniewski JP. 2011. Portland cement, mixing water, and admixtures. Third ed. Upper Saddle River, New Jersey 07458: Pearson Education, Inc.
22. Mindess S, Young JF, Darwin D. 2002. Concrete. .
23. Neuwald AD. 2010. Water-to-cement ratio and aggregate moisture corrections. *Precast Magazine*: .
24. Provis JL and vanDeventer JSJ. 2009. Geopolymers - structure, processing, properties and industrial applications. Boca Raton: Woodhead Publishing.
25. Provis JL, Lukey GC, Van Deventer, Jannie S. J. 2005. Do geopolymers actually contain nanocrystalline zeolites? a reexamination of existing results. 17:3075-85.
26. Rattanasak U and Chindaprasirt P. 2009. Influence of NaOH solution on the synthesis of fly ash geopolymer. 22:1073-8.
27. Redden R and Neithalath N. 2014. Microstructure, strength, and moisture stability of alkali activated glass powder-based binders. *Cement and Concrete Composites* 45:46+.

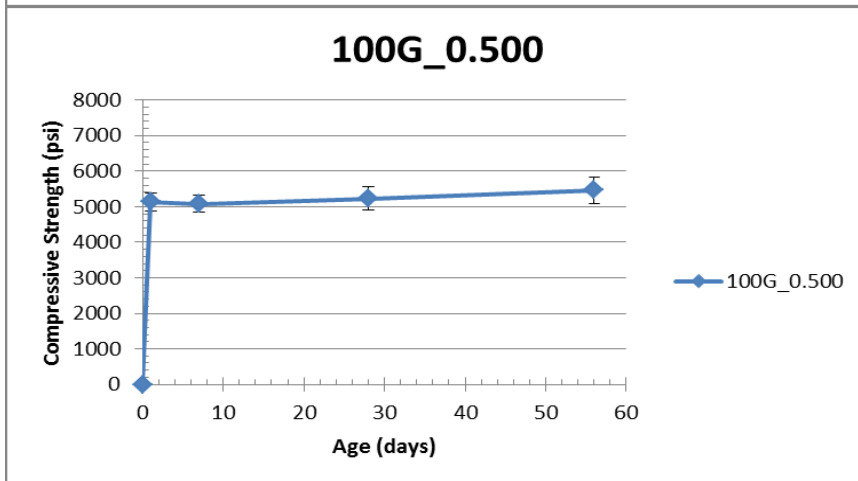
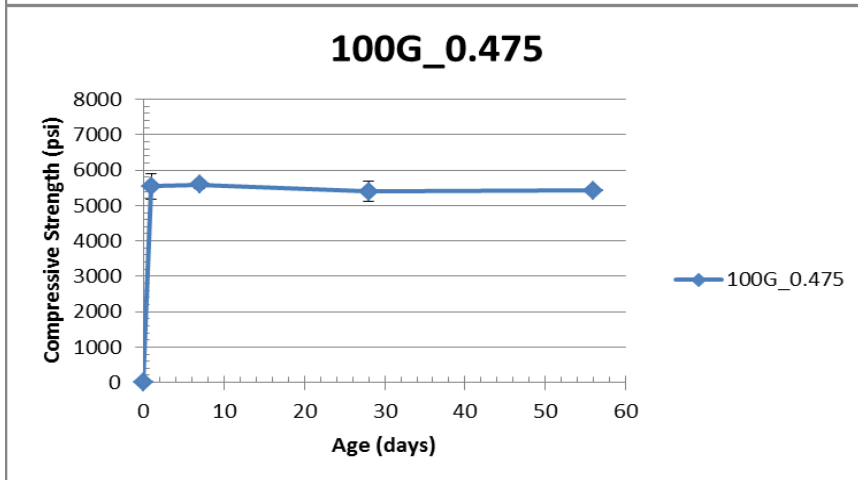
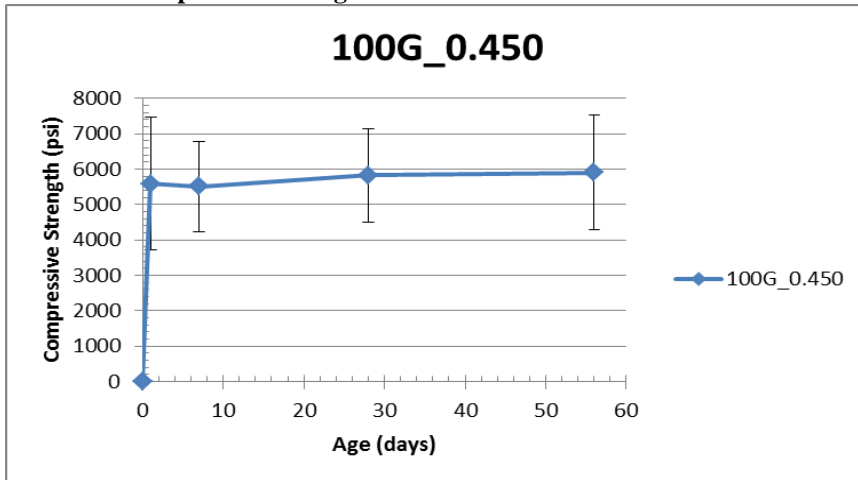
28. Shi C, Jimenez AF, Palomo A. 2011. New cements for the 21st century: The pursuit of an alternative to portland cement. 41:750-63.
29. Shi C, Jiménez AF, Palomo A. 2011. New cements for the 21st century: The pursuit of an alternative to portland cement. *Cem Concr Res* 41(7):750-63.
30. Sofi M, van Deventer JSJ, Mendis PA, Lukey GC. 2007. Engineering properties of inorganic polymer concretes (IPCs). *Cem Concr Res* 37(2):251-7.
31. Steveson M and Sagoe-Crentsil K. 2005. Relationships between composition, structure and strength of inorganic polymers : Part 2 fly ash-derived inorganic polymers. 40:4247-59.
32. Sun P and Wu H. 2013. Chemical and freeze–thaw resistance of fly ash-based inorganic mortars. *Fuel* 111(0):740-5.
33. The Science of Concrete [Internet]; c2008 [cited 2015 . Available from: <http://iti.northwestern.edu/cement/index.html> .
34. van Oss HG. 2014. Mineral commodity summaries 2014. U.S. Geological Survey .
35. Wyoming Analytical Laboratories. 2014. Material composition analysis. .
36. Zuhua Z, Xiao Y, Huajun Z, Yue C. 2009. Role of water in the synthesis of calcined kaolin-based geopolymer. *Appl Clay Sci* 43(2):218-23.

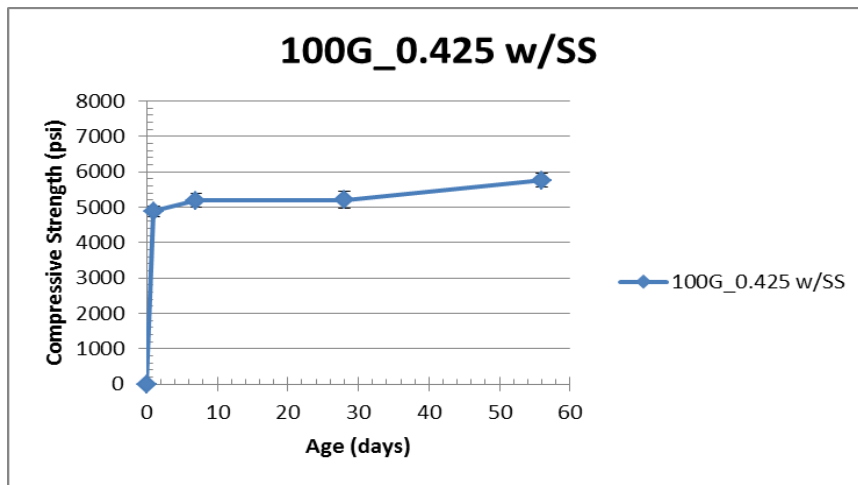
7 Appendix A

Mixture design spreadsheet example

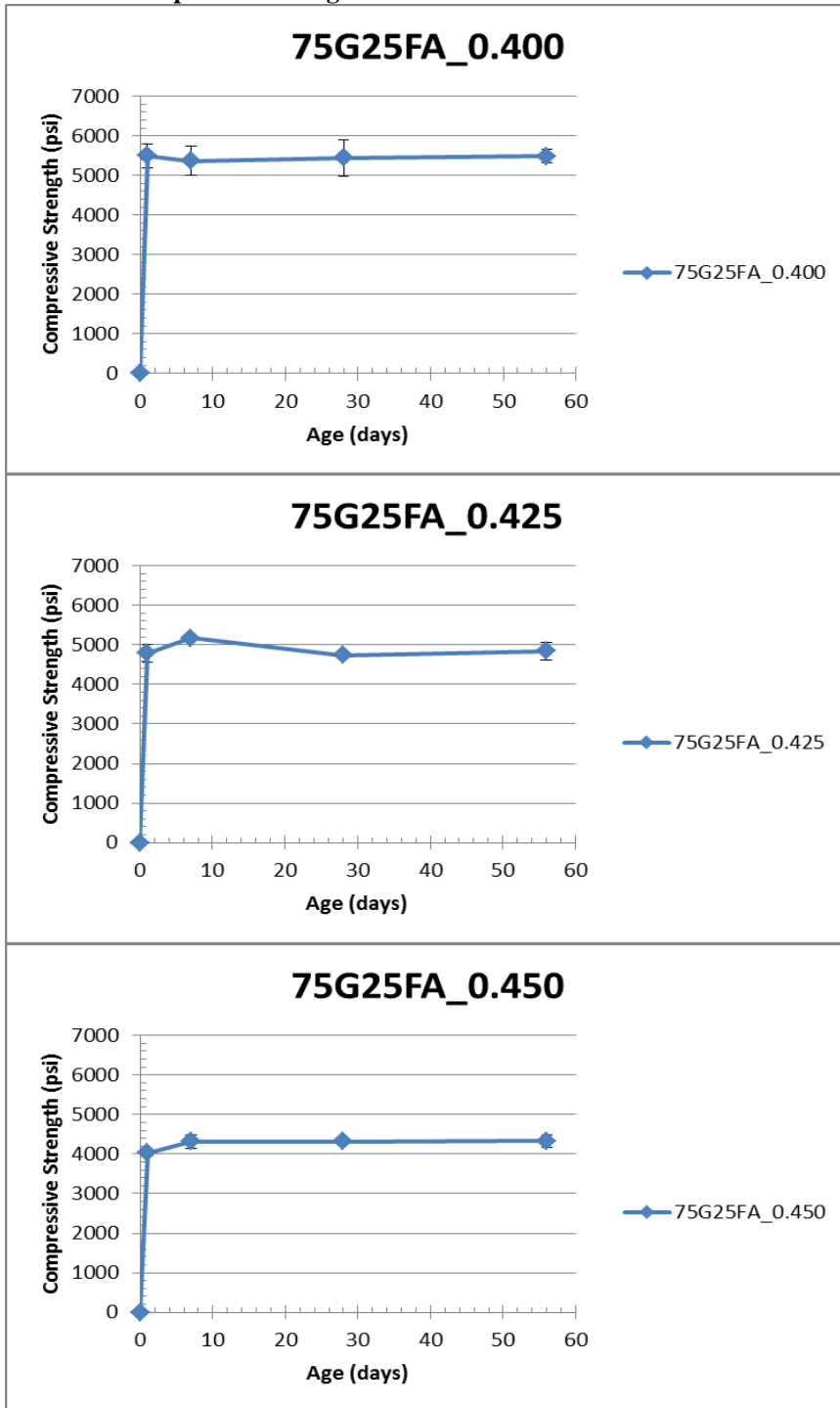
100G_0.450		
Cylinder Specimen Numbers	1-12	
Mix Type =	Mortar Ottawa	
Batch size (g) =	6000.0	
Aggregate/Aluminosilicate =	3	
Activator/Aluminosilicate Ratio by Mass =	0.5	
Sodium Silicate/NaOH Ratio by mass =	0	0.0
NaOH M =	10.0	
% CS-600 Glass by mass =	100%	100%
% Metakaolin by mass =	0%	0%
% Fly ash by mass =	0%	0%
% CS-400 Glass by mass =	0%	0%
Check Total = 100%	OK	
Aggregate (g) =	4000.0	
Washed sand (g) =	0.0	
Ottawa sand (g) =	4000.0	
Aluminosilicate (g) =	1333.3	1334.0
CS-600 Glass (g) =	1333.3	1334.0
Metakaolin (g) =	0.0	0.0
Fly ash (g) =	0.0	0.0
CS-400 Glass (g) =	0.0	0.0
Liquid Activator (g) =	666.7	668.6
Sodium Silicate (g) =	0.0	0.0
NaOH solution (g) =	666.7	668.6
NaOH flake (g) =	190.5	191.0
Water (g) =	476.2	477.6
Extra water for stoichiometry (g) =	148.0	148.9
Extra water for workability (g) =	0.00	0.0
Water/Solids Ratio by mass =	0.450	0.452
Total (molar)		
SiO ₂ /Al ₂ O ₃ =	8.39	8.39
Na ₂ O/Al ₂ O ₃ =	1.61	1.61
Na ₂ O+K ₂ O/Al ₂ O ₃ =	1.62	1.62
Na ₂ O/SiO ₂ =	0.19	0.19
CaO/SiO ₂ =	0.39	0.39
H ₂ O/Na ₂ O =	14.4	14.4
SiO ₂ =	13.37	13.38
Al ₂ O ₃ =	1.59	1.59
Na ₂ O =	2.57	2.58
K ₂ O =	0.01	0.01
Na ₂ O + K ₂ O =	2.58	2.59
H ₂ O =	37.03	37.16
CaO =	5.16	5.17

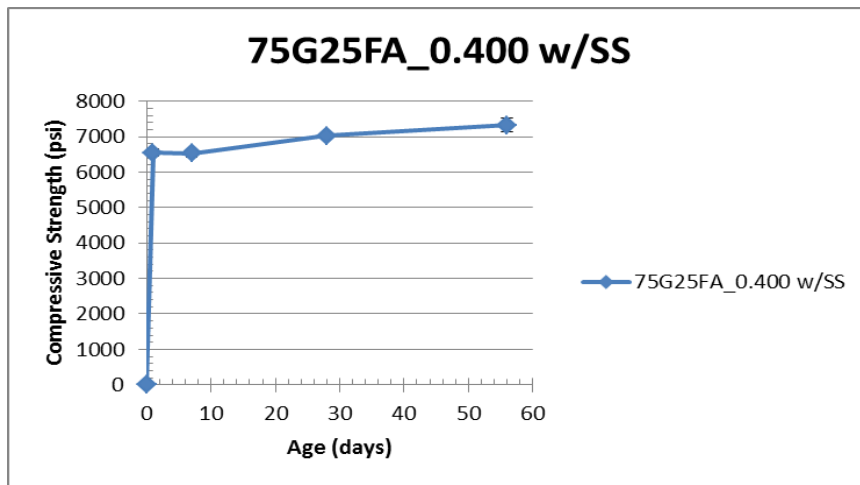
Individual compressive strength curves for 100G



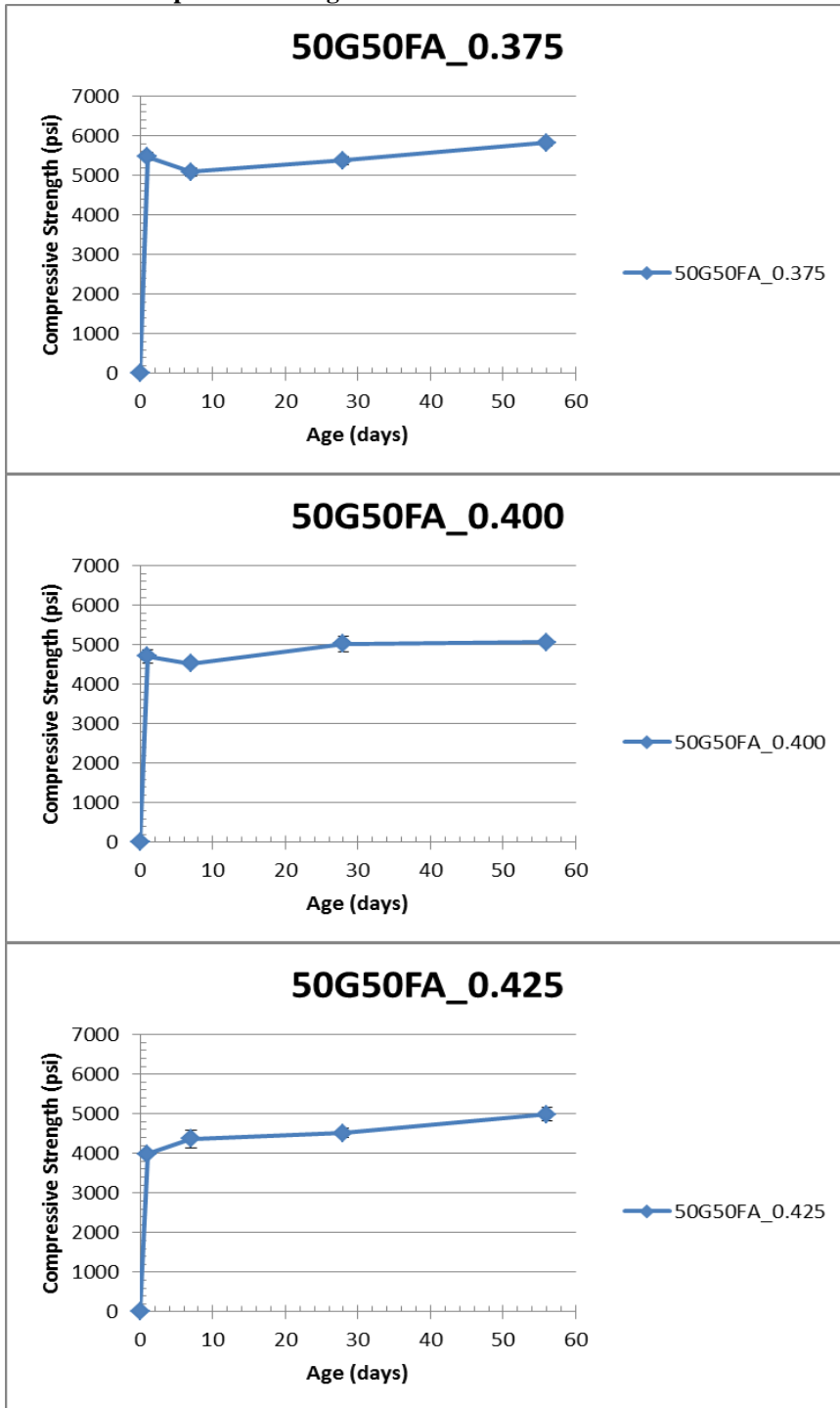


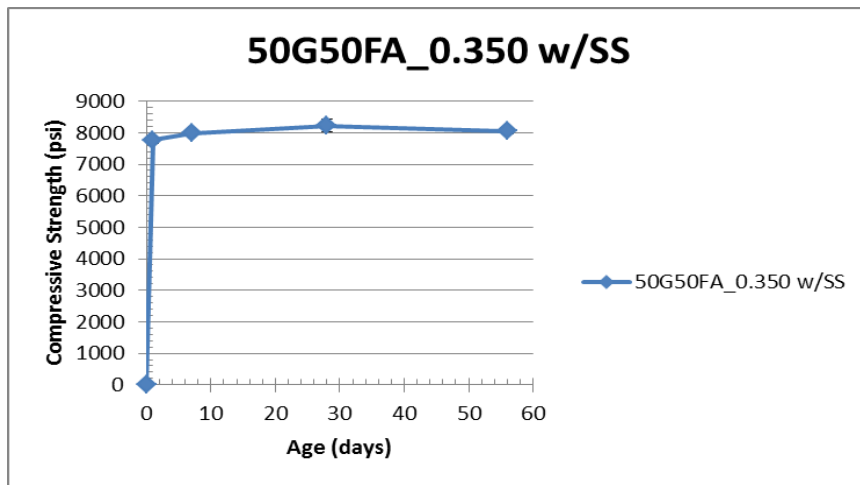
Individual compressive strength curves for 75G25FA



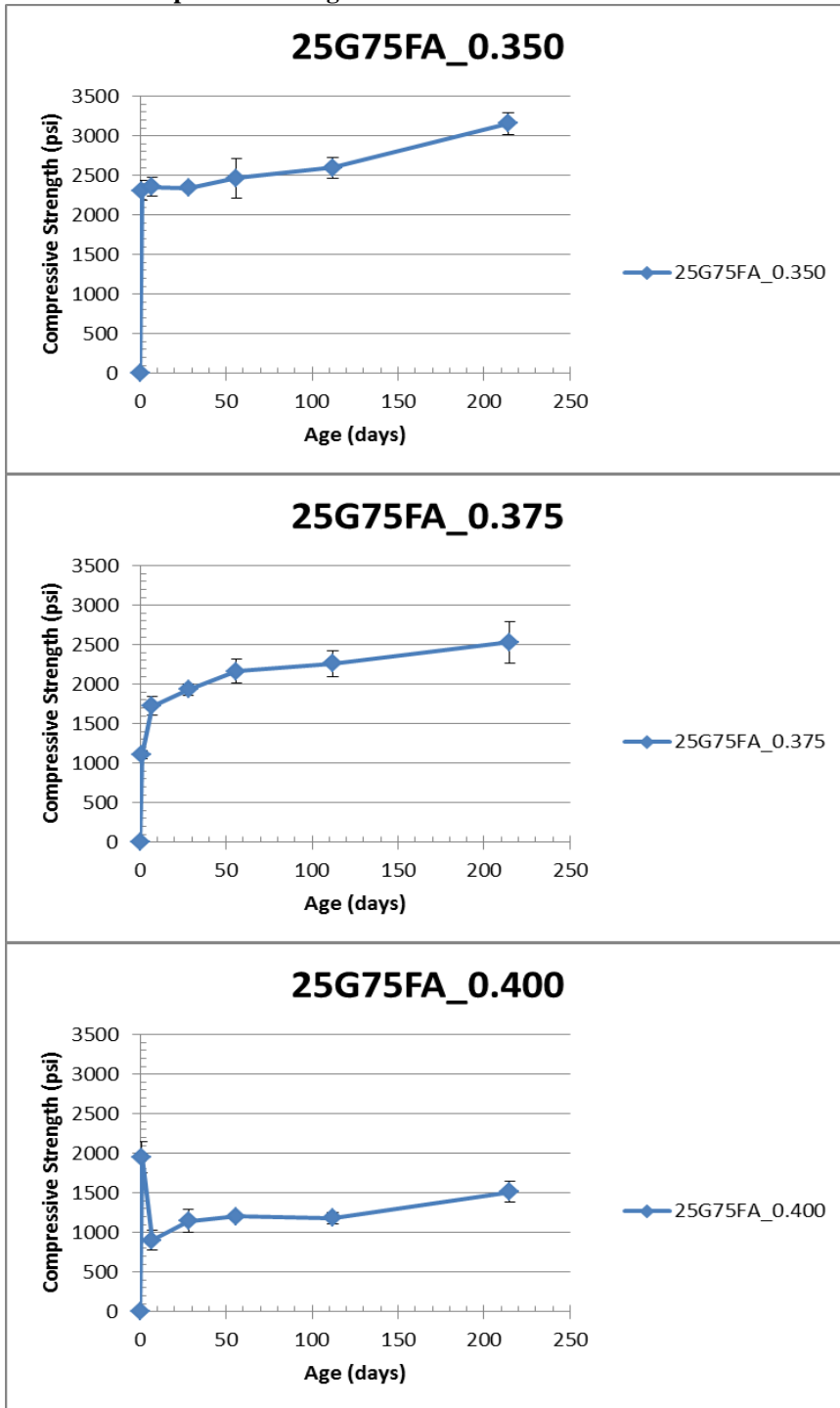


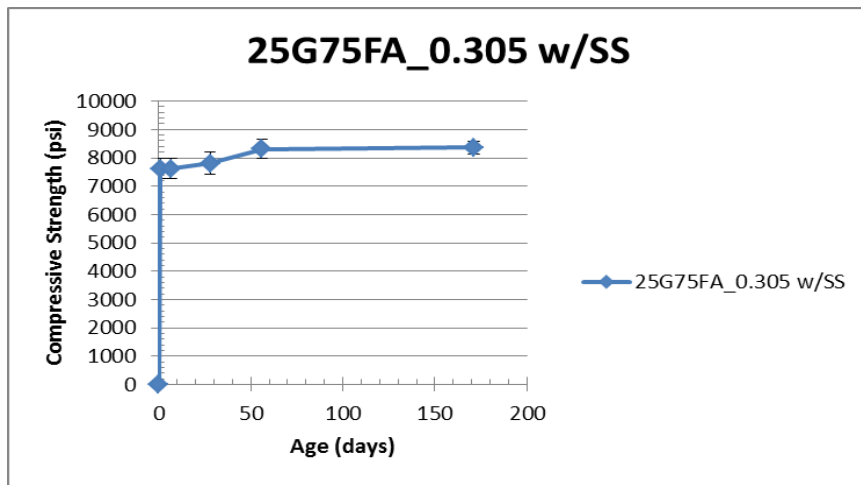
Individual compressive strength curves for 50G50FA



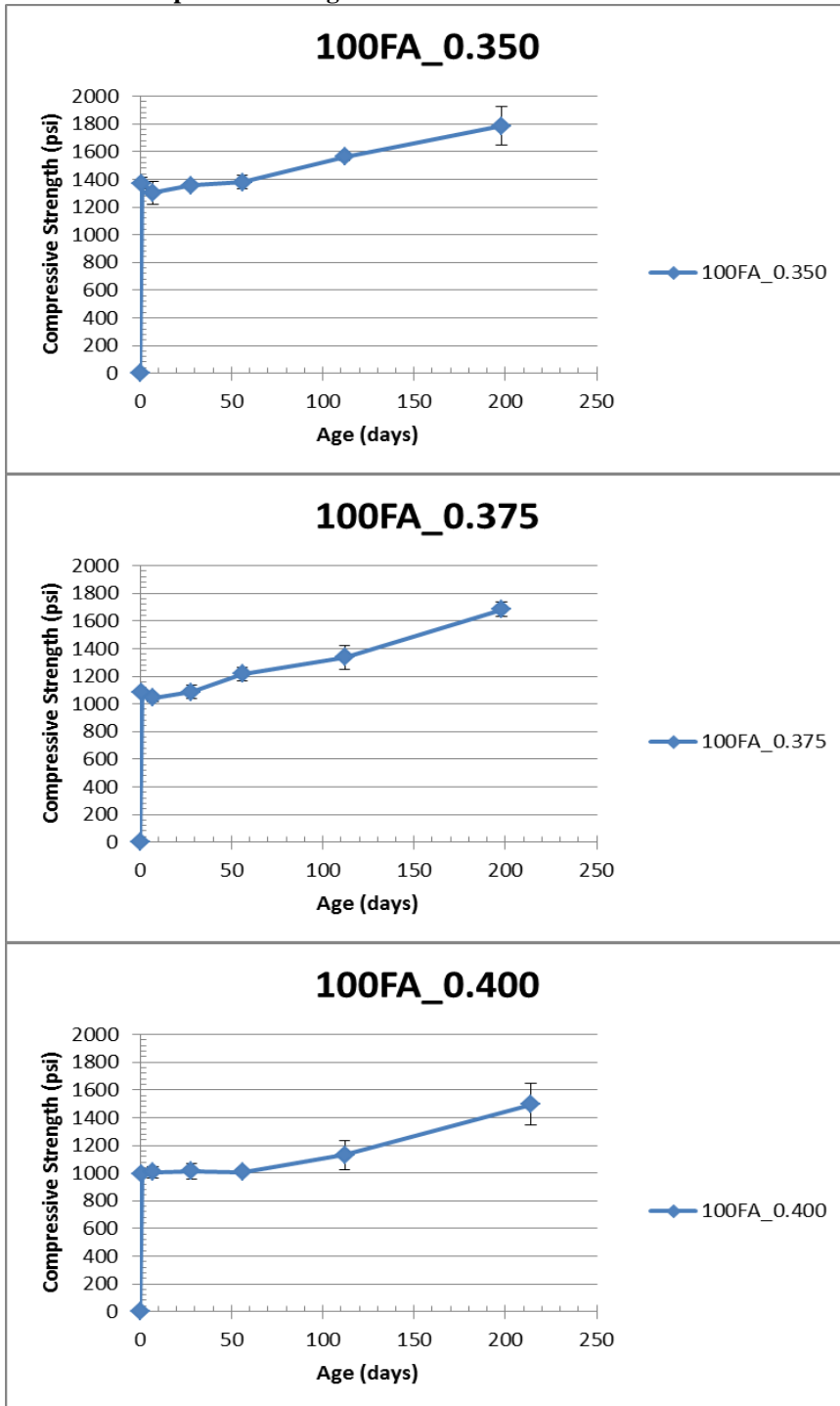


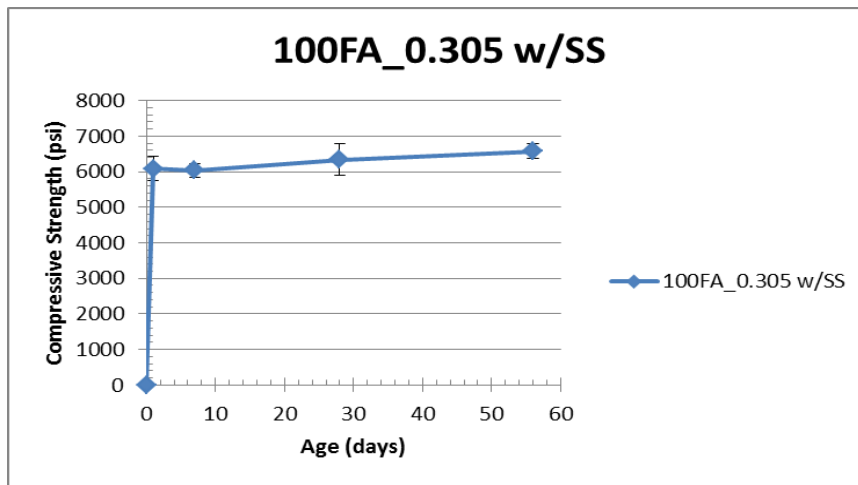
Individual compressive strength curves for 25G75FA





Individual compressive strength curves for 100FA





Compressive strength vs. W/S ratio for 1, 28, and 56 days

